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of the
AMERICAN CHEMICAL SOCIETY
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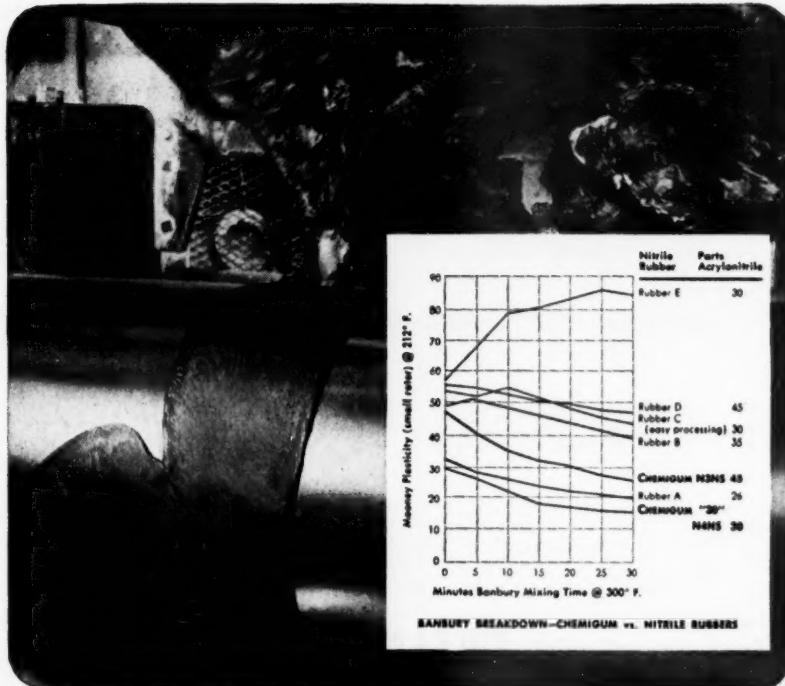
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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY, CINCINNATI, OHIO, APRIL 30 TO MAY 2, 1952

The 60th Meeting of the Division of Rubber Chemistry was held in Cincinnati, April 30 to May 2, 1952, with headquarters at the Hotel Netherlands Plaza.

The meeting was attended by about 850 registered members and guests.

The 25-Year Club met, under the Chairmanship of A. C. Eide, with 150 members present at the luncheon. The Banquet in The Hall of Mirrors, Netherlands Plaza Hotel, was attended by 550. Mayor C. W. Rich of Cincinnati, Senator Estes Kefauver, and Harold E. Stassen spoke. Dr. W. L. Semon presided at the sessions, and at the Banquet announced that the Charles Goodyear award had been made to H. E. Simmons, formerly President of the University of Akron.

The following papers were presented:

Chlorosulfonated Polythene. I. A New Elastomer. R. E. BROOKS, D. E. STRAIN, AND A. McALEVEY (E. I. du Pont de Nemours & Co., Wilmington, Del.). Chlorosulfonated Polythene. II. Metal Oxide Curing Systems. M. A. SMOOK,

I. D. ROCHE, W. B. CLARK, AND O. G. YOUNGQUIST (E. I. du Pont de Nemours & Co., Wilmington, Del.).

Chlorosulfonated Polythene. III. Organic Curing Agents. W. F. BUSSE AND M. A. SMOOK (E. I. du Pont de Nemours & Co., Wilmington, Del.). Permeability of Rubber to Organic Liquids. WILLIAM J. MUELLER (Battelle Memorial Institute, Columbus, Ohio).

The Relationship Between the Modulus of Reinforced Rubber Compounds and the Physical Properties of Various Carbon Blacks. M. L. STUDEBAKER (Phillips Chemical Co., Bartlesville, Okla.).

Alkaryl Sulfonates as Conditions in Wet Twisting Cotton Tire Cord. J. C. AMBELLANG, J. A. SHOTTON, G. W. GOOTSCHALK, H. P. STEVENS, AND G. E. P. SMITH, JR. (Firestone Tire & Rubber Co., Akron, Ohio).

The Use of the Beta Ray Gauge in the Rubber Industry. GEORGE B. FOSTER (Industrial Nucleonics, Columbus, Ohio).

Hydrocarbon Composition of Rubber Processing Oils. STEWART S. KURTZ, JR., AND CHARLES G. MARTIN (Sun Oil Co., Norwood, Pa.).

The Effects of Oils in Rubber. IRA WILLIAMS (J. M. Huber Corp., Borger, Tex.).

Reclaiming Agents for Synthetic Rubber. II. R. R. BENNETT, H. E. ALBERT, J. C. AMBELLANG, W. S. COOK, O. E. P. SMITH, JR., AND F. J. WEBB (Firestone Tire and Rubber Co., Akron, Ohio).

Ebonite from Hevea Latex. R. HOUWINK AND J. W. F. VAN'T WOUT (Rubber-Stichting, Delft, Holland).

Polymerization Stopping Agents. C. J. ANTILFINGER AND C. H. LUFTER (B. F. Goodrich Chemical Co., Akron, O.).

Physical Properties of Sodium-Catalyzed Polymers. W. K. TAFT, M. H. REICH, AND R. E. SCHNEIDER (Government Laboratories, University of Akron).

Polymerization Reactions with Alfin Catalysts. H. LEVERNE WILLIAMS AND R. A. STEWART (Polymer Corporation Ltd., Sarnia, Ontario, Canada).

Bound Rubber Formation in Diene Polymers. P. B. STICKNEY, E. E. MC SWEENEY, W. J. MUELLER, AND S. T. PALINCHAK (Battelle Memorial Institute, Columbus, Ohio).

Bound Rubber and Physical Properties of Diene Polymers. S. T. PALINCHAK, E. E. MC SWEENEY, W. J. MUELLER, AND P. B. STICKNEY (Battelle Memorial Institute, Columbus, Ohio).

Lead, Copper, and Bismuth Oxides as Aids in the Vulcanization of Coprecipitates of Natural Rubber and Lignin. T. R. GRIFFIN AND D. W. MAC GREGOR (National Research Council, Canada).

A Study of the Oxidation of Rubber by Means of the Isotopic Method. A. D. KIRSCHENBAUM AND A. G. STRENG (The Research Institute of Temple University and Lee Rubber & Tire Co.).

Effect of Oxygen Concentration on the Aging of Rubber Vulcanizates. I. The Effect of Partial Pressure of Oxygen on the Rate of Oxygen Absorption. WILLIAM L. COX AND J. REID SHELTON (Case Institute of Technology, Cleveland, Ohio).

Effect of Oxygen Concentration on the Aging of Rubber Vulcanizates. II. The Effect of the Partial Pressure of Oxygen on the Changes in Physical Properties Accompanying Oxidation. J. REID SHELTON AND WILLIAM L. COX (Case Institute of Technology, Cleveland, Ohio).

Products of Oxidation of an Olefin Structurally Related to GR-S. G. R. MITCHELL (Olin Industries, New Haven, Conn.) AND J. REID SHELTON (Case Institute of Technology, Cleveland, Ohio).

A Water Bomb for Studying the Oxidation of Elastomers. **Wm. M. HAINES, JR. AND H. H. GILLMAN** (Gates Rubber Company, Denver, Colo.).
Photomicrography of Progressive Ozone Cracking in Rubber Stocks. **W. G. MAYES AND MARIE L. BARZAN** (Chemical and Physical Research Laboratories Firestone Tire & Rubber Co., Akron, Ohio).
An Apparatus for the Evaluation of Ozone Protective Agents for Elastomers under Dynamic Conditions. **K. E. CREED, JR., R. B. HILL, AND J. W. BREED** (Monsanto Chemical Company, Nitro, West Virginia).

FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY BUFFALO, N. Y., OCTOBER 29-31, 1952

The 61st Meeting of the Division of Rubber Chemistry was held in Buffalo, October 29-31, 1952, with headquarters at the Hotel Statler.

The total registration was 806 members and guests.

The meeting started with a luncheon of the 25-Year Club, under the Chairmanship of H. F. Van Valkenburgh, at which 160 members were present, and 11 new members were welcomed.

On Thursday afternoon various plants were visited, including the Socony Vacuum Co., Sylvania Electric Products Inc., U. S. Rubber Reclaiming Co., Carborundum Co., and Niagara Mohawk Power Co. A Supplier's Cocktail Party, with J. H. Nesbit in charge, preceded the Banquet of the Division, which was attended by 650.

At the Business Meeting, R. A. Emmett, Chairman of the Teller's Committee, announced the result of the election for officers and directors: Chairman, S. G. Byam; Vice-Chairman, J. C. Walton; Secretary, C. R. Haynes; Treasurer, A. W. Oakleaf. Directors: Director-at-Large: R. B. Stringfield; Akron, C. A. Ritchie; Boston, J. L. Haas; Buffalo, C. O. Miserentino; Chicago, A. E. Laurence; Fort Wayne, C. S. Yoran; Los Angeles, G. W. Miller; New York, G. N. Vacca.

John Hoesly stated that the total membership of the Division was, at the time of the meeting, 3247, an increase of more than 350 since the end of 1951.

Section II of the Bylaws was amended, raising the dues of members to \$4.00 and of associates to \$6.50; Section IX was amended, raising subscriptions to \$7.50.

Three more revisions of the Bylaws were voted by the Executive Committee; (1) alternate for absent director to be the defeated candidate, or, if he is not available, some other member, who must be approved by the Chairman; (2) Councillors shall be full-voting members of the Executive Committee; (3) terms of the Councillors shall be three instead of two years, the terms not to run concurrently.

W. L. Semon was elected Councillor for three years, beginning January 1, 1953, with H. I. Cramer as alternate.

The death of two of our members was announced: W. S. Calcott, E. I. du Pont de Nemours & Co., and W. W. Higgins, United Carbon Co.

The 1953 meetings are to be March 18-19 in Los Angeles; May 27-29 in Boston, and September 9-11 in Chicago. In 1954 meetings will be April 11-16 in Louisville, Ky., and September 15-17 in New York.

The following papers were presented:

A Study of GR-S Synthetic Rubbers Extended with Rosin Type Acids. **L. H. HOWLAND, J. R. REYNOLDS, AND R. L. PROVOST** (U. S. Rubber Co., Naugatuck, Conn.).

The Effect of Chemical Composition of Petroleum Processing Oils on the Physical Properties of Oil-Enriched Rubbers. K. V. WEINSTOCK (General Tire & Rubber Co., Akron), E. B. STORY (Polymer Corp., Sarnia, Canada), AND J. S. SWEELY (Sun Oil Company, Norwood, Pa.).

Effect of Various Oils in the Oil-GR-S Masterbatch on the Breakdown of the Polymer. W. K. TAFT, JUNE DUKE, A. D. SNYDER, M. FELDON, AND R. W. LAUNDRIE (Government Laboratories, Univ. of Akron, Ohio).

The Processing of Oil-Extended and LTP GR-S Black Masterbatch. H. L. ERICSON AND L. D. CARVER (Witco Chemical Co.).

Preparation, Properties, and Evaluation of Diazo-Initiated Polymers. J. M. WILLIS, GLEN ALLIGER, B. L. JOHNSON, AND W. M. OTTO (Firestone Tire & Rubber Co., Akron, Ohio).

Nonionic, Anionic, and Cationic Emulsifiers in Butadiene-Styrene Copolymerizations. D. A. BEADELL, R. L. MAYHEW, R. C. HYATT (General Aniline & Chemical Corp.), A. F. HELIN AND J. M. GYENGE (Government Laboratories, University of Akron), and J. H. BOYD (Consultant).

Peroxides from Autoxidized Methyl Oleate and Linoleate as Initiators in the Preparation of Butadiene-Styrene Synthetic Rubber. DANIEL SWERN, JOSEPH E. COLEMAN, AND H. B. KNIGHT (Eastern Regional Research Laboratories, Pa.), K. T. ZILCH, H. J. DUTTON, AND J. C. COWAN (Northern Regional Research Laboratories, Ill.), AND J. M. GYENGE (Government Laboratories, University of Akron).

Tensile Properties of Films from GR-S Latex Polymerized at Low Temperatures. R. W. BROWN, W. E. MESSEY, AND L. H. HOWLAND (U. S. Rubber Co., Naugatuck, Conn.).

A Study of Electrical Contact Potentials Produced During Banbury Mixing. R. S. HAVENHILL, L. E. CARLSON, H. F. EMERY, AND J. J. RANKIN (St. Joseph Lead Co., Monaca, Pa.).

Active Carbons as Antistain Agents for Reclaimed Rubber. J. J. KEILEN AND W. K. DOUGHERTY (West Virginia Pulp & Paper Co., Charleston, S. C.).

Blends of Chlorosulfonated Polythene with Butadiene-Styrene Polymers. W. J. REMINGTON, J. J. ONDREJCIN, AND GEORGE H. BOWERS (E. I. du Pont de Nemours Experimental Station, Wilmington, Del.).

Ozone-Resistant Chlorosulfonated Polythene Blends. R. T. CURRIN, W. J. REMINGTON, AND W. B. CLARK (E. I. du Pont de Nemours Experimental Station, Wilmington, Del.).

Compounding of Silicone Rubber. II. WALTER B. SPENCER, WILLIAM B. DAVIS, AND F. L. KILBOURNE, JR. (Connecticut Hard Rubber Co.), AND JUAN MONTERMOSO (Office of The Quartermaster General, Washington, D. C.).

Purchase and Inspection Standards for Dry Natural Rubber. W. J. SEARS (Rubber Manufacturers' Association, New York) AND C. O. MISERENTINO (Dunlop Tire & Rubber Co., Buffalo).

Charles Goodyear Lecture, "Out of the Past." H. E. SIMMONS.

Characterization of Cord Fatigue in Tires. K. R. WILLIAMS, J. W. HANNEL, AND J. M. SWANSON (E. I. du Pont de Nemours & Co., Richmond, Va.).

Study of the Factors Affecting the Friction of Tread Compounds on Ice. C. S. WILKINSON, JR. (Goodyear Tire & Rubber Co., Akron, Ohio).

Behavior of Motor-Mounting Compounds Under Continuous Shear Load. G. I. HALL, F. S. CONANT, AND J. W. LISKA (Firestone Tire & Rubber Co., Akron, Ohio).

Electrical Conductivity of Rubber Carbon-Black Vulcanizates. B. B. S. T. BOONSTRA AND E. M. DANNEBERG (Godfrey L. Cabot Co., Boston).

Cross-Linking in Natural-Rubber Vulcanizates. H. E. ADAMS AND B. L. JOHNSON (Firestone Tire & Rubber Co., Akron, Ohio).

Chemical Analysis of GR-S by Complete Solution Procedures. FREDERIC J. LINNIG, JEAN M. PETERSON, DEMBY M. EDWARDS, AND WALTER L. ACHERMAN (National Bureau of Standards, Washington, D. C.).

A Quantitative Study of the Reaction of Ozone with GR-S Rubber and Various Antioxidants. E. R. ERICKSON, R. A. BERNTSEN, AND E. L. HILL (Augusta Research Foundation, Ill.).

The Permeability of Different Elastomers. A. D. KIRSHENBAUM, A. G. STRENG (Research Institute of Temple University), AND W. B. DUNLAP, JR. (Lee Rubber & Tire Corp., Conshohocken, Pa.).

Vulcanization Using Sulfur 35. I. AUERBACH (Goodyear Tire & Rubber Co., Akron, Ohio).

Discussion of the Triangular-Phase Diagram for Copolymer Solvent Systems. F. W. BOGGS (General Laboratories, U. S. Rubber Co., Passaic, N. J.).

Second-Order Transition Temperature of Butadiene Copolymers. R. H. GERKE (General Laboratories, U. S. Rubber Co., Passaic, N. J.).

C. R. HAYNES, Secretary

VIBRATION CHARACTERISTICS OF TREAD STOCKS *

K. E. GUI, C. S. WILKINSON, JR., AND S. D. GEHMAN

THE GOODYEAR TIRE AND RUBBER CO., AKRON, OHIO

One of the most distinctive features of the vibration of tread stocks is a dependence of the dynamic modulus and internal friction on the amplitude. This has been consistently observed over a wide range of experimental conditions.¹ For gum stocks, these effects are so small that they have usually escaped detection. However, analogous effects with gum stocks of a magnitude of a few per cent have been reported, and it is very probable that they exist. In contrast, nonlinear vibration characteristics for tread stocks are so pronounced that they must be taken into account in any dynamic testing procedure for evaluating tread compounds, and also in any precise effort to estimate the effective hardness of tire treads on the road.

These phenomena with tread stocks are of particular interest because of their puzzling nature, the difficulty in formulating any exact explanation for them, and the possibility that a better understanding of them may lead to new information on molecular deformation mechanisms and structural details of tread stocks.

The more obvious explanations to account for a decrease of modulus and internal friction with increasing amplitude of vibration of tread stocks have been ruled out by experimental work which has been reported. That it is not due primarily to a temperature rise of the test-piece is indicated by the experiments of Stambaugh², Gehman³, and Waring⁴. The fact that the effect occurs for shear vibrations⁵, as well as for compression vibrations⁶, eliminates any association of the effect with nonlinear static stress-strain characteristics. More evidence on these points will be given in the present paper. The occurrence with shear vibrations also excludes any explanation based on volume changes at small deformations⁷.

The effect of the time schedule or deformation history on the amplitude effects has been studied in several investigations⁸. This aspect of the phenomena points to structural mechanisms analogous to those which occur in colloidal systems showing structural viscosity. Additional reasons for this point of view will be presented, and an attempt will be made to develop the ideas more specifically than has been accomplished heretofore.

METHOD

All compression and shear experiments were made using the Goodyear Vibrotester. Since the apparatus and theory involved in its application and the procedure employed have been discussed in previous articles⁹, no extended discussion will be given here. While the instrument is capable of being oper-

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 44, No. 4, pages 720-723, April 1952. This paper represents work carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government synthetic rubber program. It was presented before the Division of Rubber Chemistry of the American Chemical Society at the Diamond Jubilee Meeting of the Society, New York, N. Y., September 4-7, 1951.

ated over a frequency range of 20 to 200 cp., all measurements reported here were made in the range of 55 to 65 cp. unless otherwise specified. Variation in modulus and resilience over this limited range of frequencies is negligible. However, as internal friction varies approximately inversely with frequency, all values for internal friction have been reduced to equivalent values at 60 cp. for purposes of comparison.

For several special experiments in which extremely small amplitudes of vibration were used, it became necessary to modify the Vibrotester by replacing the optical system for indicating amplitude with an electrical system. An inertia type of piezo-electric crystal vibration pickup was mounted on the driving axis in such a way that a voltage would be produced as the samples were oscillated. This voltage was amplified and measured by means of an electronic voltmeter.

This crystal pickup was calibrated against the regular optical system and the curve extrapolated to the low range desired.

COMPOUNDS USED

Most of the work was done using GR-S compounds, although several Hevea compounds were studied for comparison. Formulations are given in Table I. Best cures were used as indicated by ordinary tensile tests.

EXPERIMENTAL RESULTS

When a tread type of compound is vibrated over a range of increasing amplitudes and its dynamic modulus plotted as a function of amplitude, a curve such as that in Figure 1 is obtained. A part of the softening is due to the increase in temperature of the sample. An approximate correction for this can be found by combining the results of two separate experiments. First the temperature rise in a sample is measured by means of a thermocouple as its amplitude of vibration is increased. Then, in a second experiment, the sample is vibrated at a constant low amplitude as the ambient temperature is raised an amount corresponding to the increase shown in the first experiment. The decrease in modulus found here is due primarily to temperature increase, and may be subtracted from the decrease observed in the first experiment. This has been done to obtain the corrected curve shown in the figure. Since such a correction accounts for only a relatively minor proportion of the effect, none of the subsequent curves has been corrected.

The effect of amplitude of vibration on modulus may be seen over a wide range of ambient temperatures, as is shown in Figure 2. In these experiments

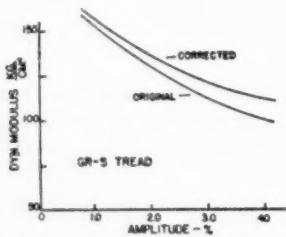


FIG. 1.—Modulus correction for temperature rise.

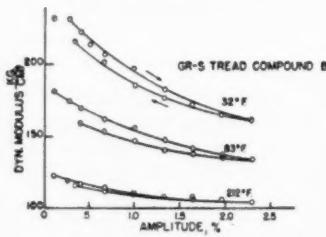


FIG. 2.—Amplitude and hysteresis effects on modulus.

TABLE I
On Continuous Terms

	Formulas of Compounds Used										O			
	A	B	C	D	E	F	G	H	I	J	K	L	M	N
GR-S, cold	100	100	100	100	100	100	70	70	100	100	100	100	90	80
GR-S, regular														
Smoked sheet														
Carbon black														
HAF	50	50	50	50	50	50	50	50	50	20	35	50	60	
EPC														
SRF														
MT														
Silica (RS-1)														
Phosphate (S6)	3	3	3	3	5	3	2.1	5	5	5	5	5	10	20
Zinc oxide	1.6	1.6	1.6	1.6	1.75	1.6	1.12	1.75	1.75	1.75	1.75	1.75	2.7	2.4
Sulfur														
Amax	0.7	0.7	0.7	0.7	0.7	0.25	0.7	0.49	0.49	0.75	0.75	0.75	1.44	1.28
Diphenylguanidine	0.7	1	1	1	1	1	1	0.7	0.7	0.25	0.25	0.25	0.25	0.56
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	1	1	0.9	0.8
Altax														
Triethanolamine													0.45	0.40

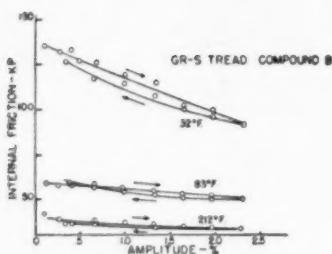


FIG. 3.—Amplitude and hysteresis effects on internal friction.

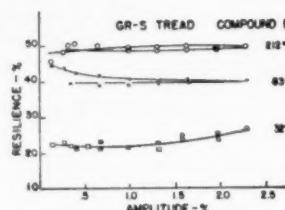


FIG. 4.—Amplitude and hysteresis effects on resilience.

the test-pieces were vibrated at each amplitude for several minutes to establish equilibrium before taking a measurement. Amplitude was increased in increments to a maximum of about 2.3 per cent and then decreased to approximately the initial value. At no time was the vibration interrupted. At all temperatures, the samples recovered most of their stiffness as the amplitude was reduced. Figures 3 and 4 show corresponding plots for internal friction and resilience. Ordinarily, dynamic modulus and internal friction both decrease with increasing amplitude, with the result that resilience, which is a function of them, remains about the same. In some instances, however, resilience may show a slight change.

Experiments showed the amplitude effect to persist at widely different frequencies. Compound B experienced a loss in dynamic modulus of 28.2 per cent as its amplitude was increased from 0.33 to 2.66 per cent, while vibrating at 160 cps. There was a corresponding loss of 27.6 per cent at 60 cps.

When a strip of this compound was used for the suspension of a torsion pendulum, the effect could be measured. The modulus for an initial vibration amplitude of $\pm 45^\circ$ was reduced to 89 per cent of its value when the initial amplitude was increased to $\pm 90^\circ$. The oscillation frequency was of the order of 0.15 cps.

The possibility of nonlinearity of the stress-strain curve contributing to the amplitude effect was investigated. Dead-weight loading of the samples while in the machine gives the curve shown in Figure 5. Sufficient time was allowed at each point to eliminate any noticeable creep. As may be seen the curve is substantially linear. It differs in this respect from the ordinary compression curve for rubber due to the system of test-pieces used¹⁰.

Careful tests were made on a Hevea tread compound to explore the amplitude effects for very low amplitudes. The results are shown in Figure 6. The

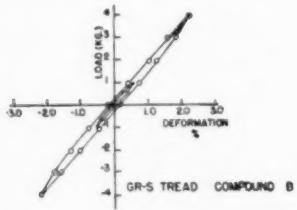


FIG. 5.—Static hysteresis loop.

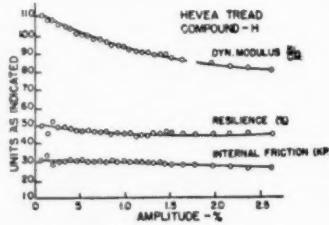


FIG. 6.—Amplitude effects on dynamic properties.

scatter of points at the small amplitude ends of the internal friction and resilience curves indicates the limit of precise measurement of amplitudes with the standard optical system. To obtain more accuracy for these low amplitudes, the work was repeated, using a crystal pickup with the results shown in Figure 7. Because of the extrapolation involved in the calibration of the pickup, the absolute magnitude of the values shown may be somewhat in error. However, there seems to be little doubt that the internal friction continues to increase for as low an amplitude as could be measured here.

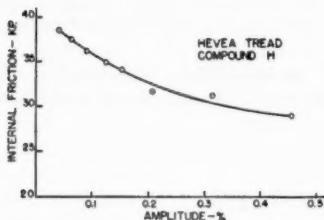


FIG. 7.—Internal friction at low amplitudes.

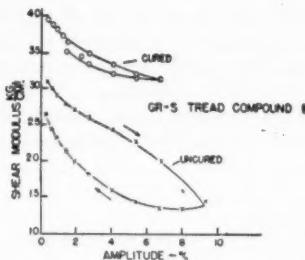


FIG. 8.—Amplitude and hysteresis effects in shear.

Results of shear vibration measurements for both raw and cured samples of compound B are given in Figure 8. Points are shown for values as the amplitude is first increased and then decreased.

Relative changes in modulus with amplitude for compounds containing equal loadings of different fillers are shown in Figure 9. The effect is most pronounced for the reinforcing type of fillers, but may be noticed also for those not generally considered as such.

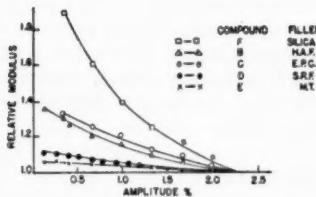


FIG. 9.—Comparison of amplitude effect for various fillers.

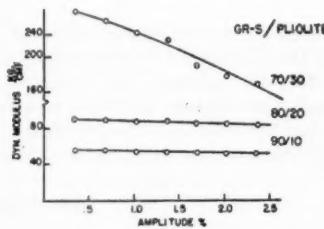


FIG. 10.—Amplitude effect with Pliolite fillers.

Figure 10 gives similar results for mixtures of GR-S and Pliolite. The effect may be greatly enhanced by increasing the amount of filler, as may be seen from these results and also those of Figure 11. Results previously published¹⁰ may be interpreted as indicating that amplitude effects become pronounced when the thickness of the rubber films between the particles approximates the particle diameter. When the rate of decrease in modulus with increasing amplitude is observed as a function of pigment loading¹⁰, it is found that there is a rather definite loading at which the rate begins to increase rapidly. The loading at which this point occurs depends on the type of pigment. The

increase in rate in the case of Superspectra black, for example, occurs at a loading of about 14 parts per 100 parts of rubber, both by weight. Points for gas black, clay, blanc fixe, and Thermatomic follow in order with loadings of 30, 60, 80, and 90 parts per hundred, respectively. Although quite small, the effect can be seen in gum compounds, as is shown in the lowest curve of Figure 11.

That the effect does not depend on the use of a sinusoidal wave form, such as is present in the resonant-type machines, is evident from the results shown in Figure 12. These data were obtained using an Instron tester¹¹. With this machine the velocity is linear throughout the cycle, changing direction very rapidly at each end of the vibration. The samples were narrow strips and were used in tension. This curve is offered to show that the effect does not depend on the shape of the test-piece and may be observed for tensile vibrations as well as compressive and shear vibrations.

That the effect may well be described as thixotropic is evident from the curve of Figure 13. The sample was vibrated for 10 minutes to reach a state

FIG. 11.—Amplitude effect on modulus at various carbon black loadings.

FIG. 12.—Amplitude effect for low-frequency, square wave-type vibration.

of equilibrium and its modulus was measured at low amplitude. The amplitude was then increased to approximately 2.5 per cent and the sample was vibrated another 10 minutes. After this, the amplitude was quickly reduced to that at which the original modulus was measured and periodic readings were taken during the following 25 minutes. The very definite recovery of stiffness is an indication of the thixotropic character of the material.

DISCUSSION OF RESULTS

Although the nonlinear phenomena studied in this work have been observed in vibration, there is good reason to suppose that the molecular mechanisms involved may be related to more general flow and deformation processes with rubber. Even ordinary liquids with elongated molecules have been reported to show temporary reductions in viscosity at high rates of shear¹². This work also was plagued with the difficulty of eliminating temperature effects, but, as with the rubber tread stocks in vibration, there were definite effects which could not be explained on the basis of temperature rise. The non-Newtonian nature of the flow of rubber solutions and raw rubber is well known¹³. Smallwood¹⁴ applied Eyring's reaction rate theory of non-Newtonian viscosity to flow curves for raw rubber with reasonable success, but did not reach an unequivocal picture of the orientation and flow processes.

To understand the nonlinear vibration effects with tread stocks, it seems most profitable to take into account the flow processes of the rubber molecules as revealed by the rheological experiments and add probable modifications, because of the environment of pigment particles.

When non-Newtonian flow is observed in a dispersed system, it is ascribed to an effect of the rate of shear on the orientation, shape, or structure of the dispersed particles. Reiner¹⁵ has given a detailed analysis of how these various mechanisms may be distinguished by rheological experiments, and has carried out such an analysis for rubber solutions in toluene.

It is not reasonable to suppose that the individual carbon black particles are appreciably deformed or altered in shape in the vibrations of tread stocks. Aggregates of the particles might be affected, but since the phenomena occur with a wide variety of pigments and also to a very small extent with gum stocks, this is not an adequate explanation. Some more general basis should be looked for. The deformable particle involved probably consists of the pigment particle and the rubber molecules which are attached to it. The particle deformation which is dependent on shearing stress is due to the flow characteristics of these rubber molecules which are attached to the pigment surface. The very small effects with gum stocks may be considered to arise from a few pigment particles or from hard entanglements of the chain molecules or "knots" in the structure, which act like deformable particles under shearing stresses.

The experimental results available can be examined from the above viewpoint to see what may be learned of the character of the temporary structural changes in tread stocks subjected to vibration. These appear to be of a complicated nature, with several deformation mechanisms occurring in varying degrees. A hysteresis effect in retracing a flow curve is usually ascribed to a breaking of particles or molecular bonds which reform after a time lag¹⁶. Since the curves secured with progressively increasing amplitudes do not coincide with those for decreasing amplitudes, a bond-breaking contribution to the effects is indicated—most probably a breaking of secondary valence bonds between rubber molecules.

The existence of such a mechanism is generally accompanied by a lower limit for the stress at which non-Newtonian behavior is observed, *i.e.*, a yield point. A lower limit for the amplitude for the occurrence of these amplitude effects with tread stocks has not been definitely observed. It would be very interesting if such a limit could be established, for it might give quantitative information on the size of the displacements and other conditions required for breaking secondary bonds. Neither have yield points been observed in the flow experiments with rubber solutions or raw rubber. Perhaps there is a continuous distribution in the strength of the secondary valence bonds so that, although bond breaking occurs in the flow experiments and in the amplitude effects, no lower limit is observed because there is no definite lower limit to the bond strengths. It is possible, on the other hand, that experiments with lower amplitudes than could be measured here might disclose a lower limit.

During vibration, a straightening and alignment of the molecules attached to the pigment particles appears to be a very probable mechanism to contribute to the amplitude effects. This mechanism is indicated by the fact that the amplitude effects show a temperature dependence, being relatively more pronounced at lower temperatures. Higher temperatures would be expected to both reduce the orienting forces by weakening the secondary valence forces and to increase Brownian motions of the molecular segments. Figure 14 is an

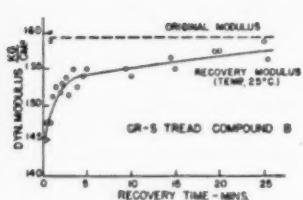


FIG. 13.—Recovery of stiffness after vibration at large amplitude.

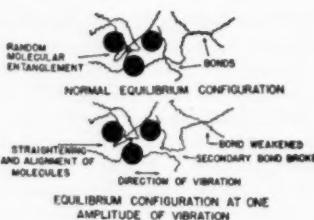


FIG. 14.—Representation of structural changes.

effort to represent pictorially the relationships between the pigment particles and the rubber molecules under normal conditions and under vibration. For each amplitude of vibration, a different system of equilibrium molecular configurations, *i.e.*, a different structure, exists. The relaxation times for these vibration-produced structures appear to be rather long, since the amplitude effects have been observed at very low frequencies. If the structural implications of these amplitude effects can be established more quantitatively, they should open up a new fascinating field for securing information on the molecular flow processes for polymers.

SUMMARY

Nonlinear vibration characteristics of tread compounds, as evidenced by a dependence of modulus and internal friction on amplitude, were studied in order to reach an understanding of these unexplained phenomena in terms of plausible structural alterations which may occur in the tread compounds because of vibration. This information is interesting both for a more exact description of the deformation processes in tread compounds, and because of the necessity of dealing with the effects in any dynamic testing procedure. Nonlinear vibration characteristics are readily observed for tread stocks of both Hevea and synthetic rubbers in the mechanical range of frequencies. Experiments were undertaken to study the extent to which these effects depend on temperature, compounding variables, and type of vibration. It may be shown that the nonlinearity is not due to temperature rise from vibration, although precise measurements are complicated by the temperature rise. The effects occur for stocks reinforced with fine silica pigment, Pliolite resin, and higher loadings of pigments generally considered to be nonreinforcing, as well as for those compounded with reinforcing blacks. The pigment loading necessary for the same degree of nonlinearity increases with the pigment size. The effects are observed in unvulcanized tread stocks and occur for vibrations in both shear, compression, and tension. Measurements of the nonlinearity for tread stocks over a range of temperatures suggest that the vibration elicits structural changes in the rubber analogous to those observed in the rheology of rubber solutions and raw rubber. The nature of these changes can be interpreted by the rheological criteria of structure developed for non-Newtonian systems. Such recognized mechanisms for structural viscosity as orientation, deformation, and breaking and reforming of bonds of the flow units are useful in explaining the phenomena observed. The effects appear to be of such magnitude that they should be taken into account in any exact study of the effect of modulus on tread wear and performance.

ACKNOWLEDGMENT

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TEMPERATURE DEPENDENCE OF DYNAMIC PROPERTIES OF ELASTOMERS. RELAXATION DISTRIBUTIONS *

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The experimental measurement of dynamic mechanical properties of a rubberlike material in small sinusoidal deformations always consists of determining two independent quantities at each frequency. These two quantities can be expressed in various ways: here, as in a paper by Marvin,¹ the dynamic properties are described by G' and G'' , the real and imaginary parts of the dynamic shear modulus, or by G' and η' , where η' is the real part of the complex viscosity ($\eta' = G''/\omega$, where ω is the circular frequency). The relations between these and other properties such as damping and energy dissipation have been given by Marvin.

This paper is concerned with two procedures for treating such experimental data to facilitate interpretation and practical use. The first is a method for combining the frequency and temperature dependence of G' and G'' by introducing certain reduced variables. The second is a method for combining G' and G'' (or G' and η') and checking one against the other by the distribution function of relaxation times. Once this function is obtained, it is possible in principle to predict any sort of time-dependent behavior under small stresses.

TEMPERATURE DEPENDENCE OF DYNAMIC PROPERTIES

It has long been recognized that there is a connection between temperature and frequency dependence of dynamic mechanical properties and that a decrease in temperature is at least qualitatively equivalent to an increase in frequency. Another manifestation of the connection is that, under conditions where the frequency dependence of G' is slight, the temperature dependence is slight also, whereas a sharp change of G' with frequency is always accompanied by a sharp change with temperature.

Investigators have sometimes combined dynamic data at different frequencies and temperatures by plotting, for example, the equivalent of G' against the logarithm of the frequency and shifting the curves along the abscissa axis. However, the conditions under which such a shift would theoretically be justified have usually not been made clear. Sometimes the temperature and frequency (or time) dependence of mechanical behavior have been combined in an explicit algebraic formula², but it is unlikely that this can be successful for dynamic properties over wide ranges of either variable, since experience indicates that G' and G'' vary in too complicated a manner to fit a simple empirical equation. The method of reduced variables outlined here does not require any analytical expression for either the temperature dependence or the frequency

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dependence, though it does involve some simple assumptions about the nature of elastic and relaxation mechanisms; these are explicitly stated.

THE METHOD OF REDUCED VARIABLES

We assume that elastic energy is stored in the deformation of a rubberlike material (whether vulcanized or not) by a variety of mechanisms of the configurational or entropy-decrease type, each of which makes a contribution G_i to the instantaneous rigidity. The stress on the i th mechanism decays exponentially with relaxation time, τ_i . This scheme is equivalent to the "generalized Maxwell model"³. The dynamic properties and the steady flow viscosity, η , are then given by the following equations⁴:

$$G'(\omega) = \Sigma G_i \omega^2 \tau_i^2 / (1 + \omega^2 \tau_i^2) \quad (1a)$$

$$G''(\omega) = \Sigma G_i \omega \tau_i / (1 + \omega^2 \tau_i^2) \quad (1b)$$

$$\eta'(\omega) = \Sigma G_i \tau_i / (1 + \omega^2 \tau_i^2) \quad (1c)$$

$$\eta = \Sigma G_i \tau_i \quad (1d)$$

It is now assumed that each G_i is proportional to the absolute temperature, T (since it involves configurational or rubberlike elasticity), and to the density, ρ (since the mechanical quantities refer to a unit cube of material, and thermal expansion decreases the number of molecules, and elastic mechanisms, within this cube), and also that all τ 's have the same temperature dependence—that is, when the temperature is changed from a reference T_0 to T , every τ_i is multiplied by the same factor a_T . It follows⁵ that the dynamic properties at the two temperatures T and T_0 , are related thus:

$$G'(\omega) = (T\rho/T_0\rho_0)G'_0(\omega a_T) \quad (2a)$$

$$G''(\omega) = (T\rho/T_0\rho_0)G''_0(\omega a_T) \quad (2b)$$

$$\eta'(\omega) = (a_T T \rho / T_0 \rho_0) \eta'_0(\omega a_T) \quad (2c)$$

$$\eta = (a_T T \rho / T_0 \rho_0) \eta_0 \quad (2d)$$

where the quantities without subscript refer to temperature T and those with subscript 0 refer to the reference temperature, T_0 . Based on these equations, it is easy to define reduced variables which will be independent of temperature if our assumptions are valid:

$$\begin{aligned} G'_p &= G' T_0 \rho_0 / T \rho; \quad G''_p = G'' T_0 \rho_0 / T \rho \\ \eta'_p &= \eta' T_0 \rho_0 / a_T T \rho; \quad \omega_p = \omega a_T \end{aligned} \quad (3)$$

If G'_p , G''_p , or η'_p is plotted against ω_p , a single curve should result from data at all temperatures and frequencies.

The method may be illustrated by data for a polyisobutylene sample of molecular weight 1,200,000 obtained with a new double transducer apparatus which is described elsewhere⁶. The original data are shown in Figure 1, which depicts families of curves for G' and η' plotted logarithmically against $\log \omega$ at different temperatures. The reduction factors a_T for temperatures other than 25° C (which is chosen as standard) must be found empirically; this is done by plotting $\log \eta' T_0 \rho_0 / T \rho$ against $\log \omega$ and shifting the curves along a line with a slope of -1 until they coincide⁷; the distance moved in either the horizontal or

vertical direction is $\log a_T$. The values of a_T thus determined, when used to calculate the reduced variables, G'_p , η'_p , and ω_p , provide a single composite curve not only for η' but also for G' (Figure 2).

The values of a_T are plotted logarithmically against the absolute temperature in Figure 3. The plot is not a straight line, so the temperature dependence of a_T is not a simple exponential function. For an unvulcanized rubber, like polyisobutylene, the temperature dependence of a_T is related to that of the

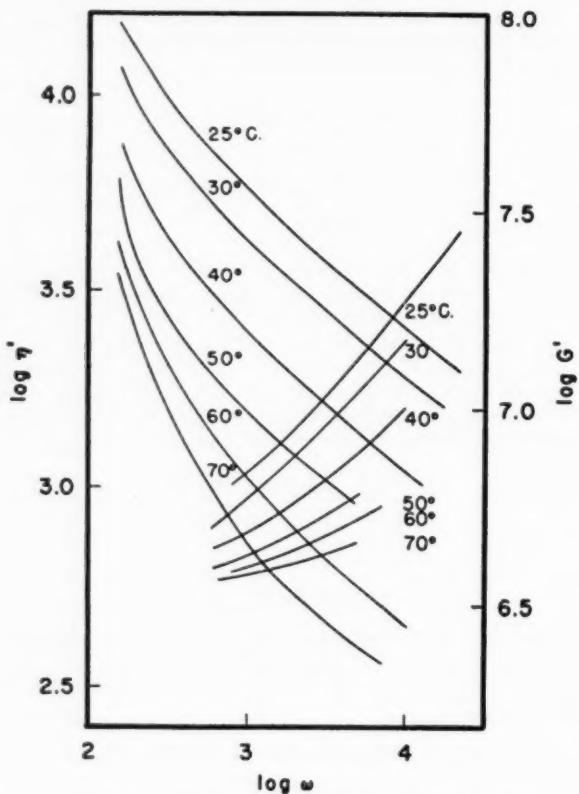


FIG. 1.—Dynamic rigidity (ascending curves) and dynamic viscosity (descending curves) of polyisobutylene, molecular weight 1,200,000, at various temperatures, plotted logarithmically against circular frequency.

steady flow viscosity; from Equation 2d, $\eta_T/\eta_0 = a_T T \rho / T_0 \rho_0$. This relation has in fact been found to hold within experimental error for polyisobutylene⁸, and it provides an alternative method for obtaining the reduction factor a_T .

Composite curves such as those of Figure 2 may be used to predict dynamic properties outside the temperature and frequency ranges of measurement. A further generalization and a check of one curve against the other is provided by the distribution function of relaxation times.

RELAXATION DISTRIBUTION FUNCTION

It is now generally accepted that the time-dependent mechanical behavior of a rubberlike material cannot be described in terms of a small number of relaxation times, corresponding to a mechanical model of a small number of springs and dashpots; the most useful description is by a continuous distribution of relaxation times, corresponding to a mechanical model of infinite extent. From such a distribution function can be calculated, in principle, the behavior under any kind of time-dependent stresses of small magnitude, including the sinusoidally varying stresses used in most dynamic measurements as well as more complicated loading patterns which may be of practical interest.

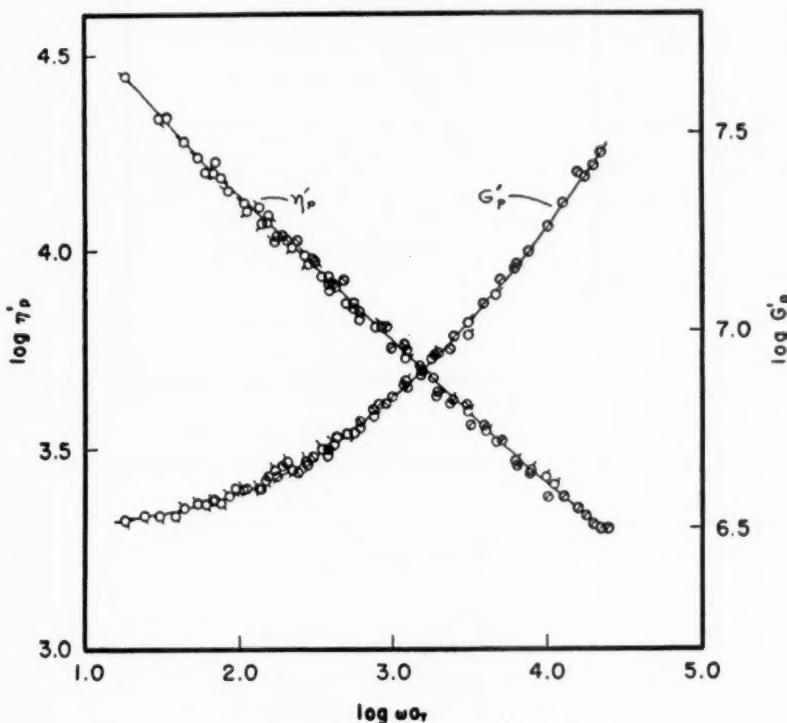


FIG. 2.—Data of Figure 1 plotted with reduced variables.

The distribution function employed here is $\Phi d \ln \tau$, which represents the differential contribution to rigidity with relaxation times lying between $\ln \tau$ and $\ln \tau + d \ln \tau$. Andrews⁹ refers to a similar function for contributions to Young's modulus, which under most conditions is greater than Φ by a factor of 6.91.

There are exact equations expressing experimental dynamic properties in terms of Φ , obtained from Equations 1a-1d by replacing the summations by

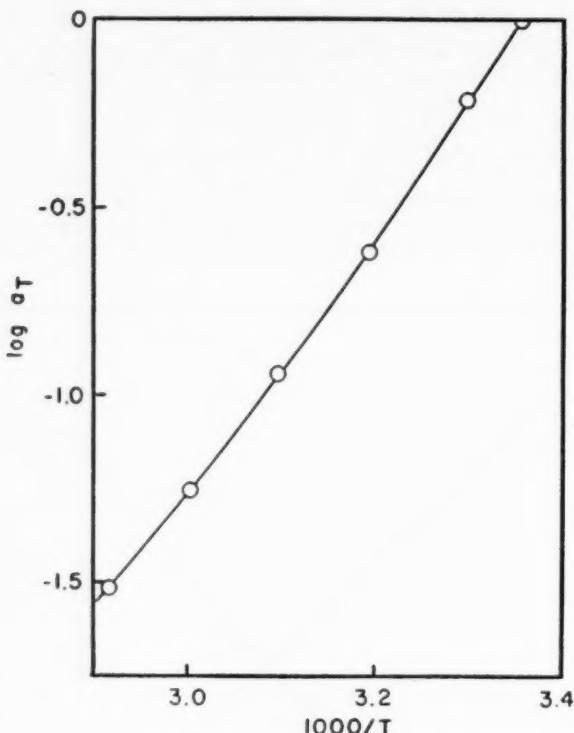


FIG. 3.—Logarithm of reduction factor a_T plotted against reciprocal absolute temperature.

integrals:

$$G' = \int_{-\infty}^{\infty} \Phi \omega^2 \tau^2 / (1 + \omega^2 \tau^2) d \ln \tau \quad (4a)$$

$$G'' = \int_{-\infty}^{\infty} \Phi \omega \tau / (1 + \omega^2 \tau^2) d \ln \tau \quad (4b)$$

$$\eta' = \int_{-\infty}^{\infty} \Phi \tau / (1 + \omega^2 \tau^2) d \ln \tau \quad (4c)$$

It is not so easy, however, to obtain Φ from the experimental quantities; ordinarily approximation methods are employed. A first approximation method which has been used for the real part of the dynamic Young's modulus by several authors¹⁰ and has been extended⁷ to G' , G'' , and η' , as well as a new second approximation method, are outlined here. Another type of approximation has been recently recommended by ter Haar¹¹. Unfortunately, this method is successful only when Φ is inversely proportional to τ , which is the case ter Haar happens to choose as an illustration; for other cases it gives highly erroneous results.

CALCULATION OF Φ —FIRST APPROXIMATION

The range of integration in Equation 4a may be divided into three regions: where $\tau \ll 1/\omega$, the integrand is practically zero; where $\tau \sim 1/\omega$, the integrand is finite but less than Φ ; where $\tau \gg 1/\omega$, the integrand is practically equal to Φ . If the distribution is broad, the last region will contribute most of the integral, which can, therefore, be approximated by $\int_{-\ln \omega}^{\infty} \Phi d \ln \tau$. Differentiation with respect to the lower limit of this expression gives an explicit formula for Φ in terms of G' . Similar treatment of the other dynamic properties yields the following first approximation formulas⁷:

$$\Phi(-\ln \omega) = G'(d \log G'/d \log \omega) \quad (5a)$$

$$\Phi(-\ln \omega) = G''(1 - d \log G''/d \log \omega) \quad (5b)$$

$$\Phi(-\ln \omega) = -\omega \eta'(d \log \eta'/d \log \omega) \quad (5c)$$

The value of Φ corresponding to a given τ may thus be calculated from the slope of a log-log plot of any dynamic property against frequency, measured at the value of ω which is the reciprocal of τ . To the extent that this first approximation is valid the experimental data are accurate, the calculations of Φ from G' and from G'' or η' should agree. Values obtained from the curves of Figure 2, representing the function as reduced to 25° C, are plotted in Figure 4 and show good agreement. In other cases, however, discrepancies of 20 per cent

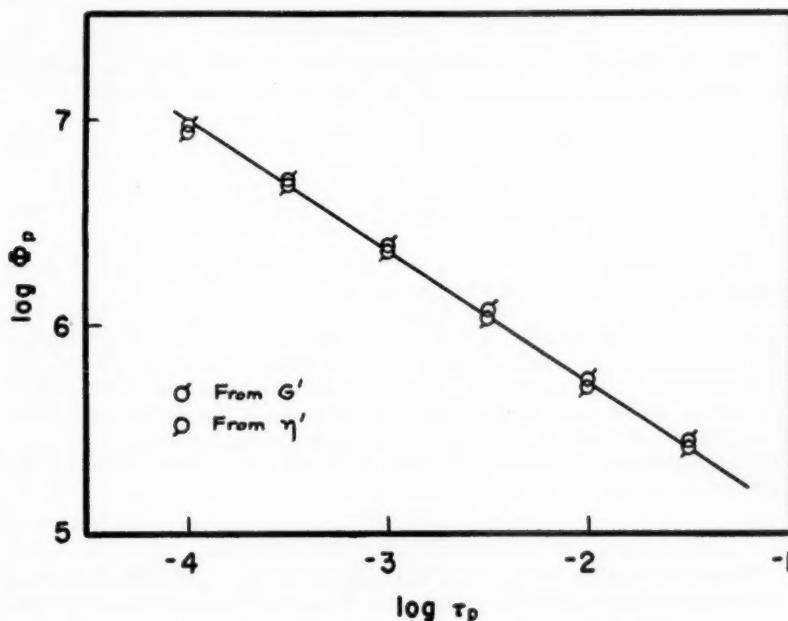


FIG. 4.—Logarithmic distribution of relaxation times as derived in first approximation from dynamic rigidity and from dynamic viscosity.

or greater have been observed between Φ values from the two experimental sources. Experimental measurements have now progressed to the point where this is beyond experimental error, and an improved calculation is therefore desirable.

CALCULATION OF Φ —SECOND APPROXIMATION

It is found experimentally that Φ as derived by the first approximation is often a simple power function of τ over a range of several powers of ten. Thus, the straight line in Figure 4 corresponds to $\Phi = k\tau^{-0.6}$ from $\tau = 10^{-4}$ to $\tau = 10^{-1.5}$ second. This region has been previously identified in polyisobutylene from earlier measurements⁷. At much longer times, on the other hand, as shown by stress relaxation measurements⁹, Φ is flat, corresponding to $k\tau^0$. At still longer times, it again decreases with increasing τ .

To obtain a second approximation, it is assumed that within a limited region Φ may be represented by the power law $\Phi = k\tau^{-m}$. Exact expressions for G' , G'' , and η' are derived from this by Equations 4a to 4c, and then the cycle is completed by substituting these expressions into the approximate Equations 5a-5c. The resulting values of Φ differ from the initial power law only by numerical factors which are functions of m . It may be assumed that the values obtained by applying Equations 5a-5c to experimental data are in error by the same factors, which can then be used to obtain the corrected second approximations:

$$\Phi(-\ln \omega) = AG'(d \log G'/d \log \omega) \quad (6a)$$

$$\Phi(-\ln \omega) = BG''(1 - d \log G''/d \log \omega) \quad (6b)$$

$$\Phi(-\ln \omega) = -C\omega\eta'(d \log \eta'/d \log \omega) \quad (6c)$$

The correction factors are obtained as gamma functions of m , the negative slope measured on the log-log plot¹² of the first approximation Φ against τ :

$$A = (2 - m)/2\Gamma\left(2 - \frac{m}{2}\right)\Gamma\left(1 + \frac{m}{2}\right) \quad (7a)$$

$$B = C = (1 + m)/2\Gamma\left(\frac{3}{2} - \frac{m}{2}\right)\Gamma\left(\frac{3}{2} + \frac{m}{2}\right) \quad (7b)$$

It turns out that, for $m = 0.5$, $A = C = 0.90$, which explains the fortuitous agreement shown in Figure 4 where $m = 0.6$.

Equations 6a-6c should be good approximations except in regions where the value of m changes sharply. On the low τ side of such a bend in the log-log plot of Φ against τ , the value from G'' or η' (Equation 6b or 6c) will be most nearly correct; on the high τ side of such a bend, the value from G' (Equation 6a) will be preferable. From these considerations, it should be possible to obtain the function Φ from dynamic data with adequate accuracy. A more detailed discussion, with tables of values of A and B , has been submitted for publication elsewhere¹².

APPLICATIONS OF FUNCTION Φ

When the function Φ has been determined, it may be used to calculate various properties, including G' , G'' , and η' , as functions of frequency; the steady flow viscosity (for unvulcanized rubbers); the elastic energy stored in steady flow, as a function of shear stress; the extent of elastic recovery on

release of stress following cessation of steady state of flow; the course of stress relaxation following sudden strain; and the course of stress relaxation following cessation of steady flow. These are illustrated in Table I as both exact and approximate integrals. The latter and some of the former are easily evaluated graphically¹³, though some of the exact forms would be tedious without computing aids.

Attempts¹⁴ to use simple analytical expressions for Φ in formulas such as these may lead to quite erroneous results unless the applications are carefully restricted to conditions where these expressions are valid. Over wide ranges of τ , Φ varies in a complicated manner, and it is believed preferable to rely on graphical methods using experimental data directly.

TABLE I
CALCULATION OF MECHANICAL BEHAVIOR FROM Φ

Property	Exact formula	Approximate formula
Dynamic rigidity, real (G')	Eq. 4a	$\int_{-\ln \infty}^{\infty} \Phi d \ln \tau$
Dynamic rigidity, imaginary (G'')	Eq. 4b	$\omega \int_{-\infty}^{-\ln \omega} \tau \Phi d \ln \tau$
Dynamic viscosity, real (η')	Eq. 4c	$\int_{-\infty}^{-\ln \omega} \tau \Phi d \ln \tau$
Steady flow viscosity (η)	$\int_{-\infty}^{\infty} \tau \Phi d \ln \tau$	—
Elastic energy stored in steady flow (W)	$(3^2/2\eta^2) \int_{-\infty}^{\infty} \tau^2 \Phi d \ln \tau$	—
Elastic strain recovery after stress release following steady flow (γ)	$(3/\eta^2) \int_{-\infty}^{\infty} \tau^2 \Phi d \ln \tau$	—
Course of stress relaxation after sudden strain [$\mathcal{J}(t)$]	$\gamma \int_{-\infty}^{\infty} \Phi e^{-t/\tau} d \ln \tau$	$\gamma \int_{\ln t}^{\infty} \Phi d \ln \tau$
Course of stress relaxation after cessation of steady flow ^a [$\mathcal{J}(t)$]	$\dot{\gamma} \int_{-\infty}^{\infty} \tau \Phi e^{-t/\tau} d \ln \tau$	$\dot{\gamma} \int_{\ln t}^{\infty} \tau \Phi d \ln \tau$

^a Subject to non-Newtonian correction¹⁵.

Information concerning the form of the distribution function over wide ranges of time scale and its dependence on chemical composition, molecular weight, and molecular-weight distribution should be forthcoming in the near future.

SUMMARY

By the use of reduced variables, the temperature dependence and frequency dependence of dynamic mechanical properties of rubberlike materials can be interrelated without any arbitrary assumptions about the functional form of either. The definitions of the reduced variables are based on some simple assumptions regarding the nature of relaxation processes. The real part of the reduced dynamic rigidity, plotted against the reduced frequency, gives a single composite curve for data over wide ranges of frequency and temperature; this is true also for the imaginary part of the rigidity or the dynamic viscosity. The real and imaginary parts of the rigidity, although

independent measurements, are interrelated through the distribution function of relaxation times, and this relation provides a check on experimental results. First and second approximation methods of calculating the distribution function from dynamic data are given. The use of the distribution function to predict various types of time-dependent mechanical behavior is illustrated.

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NOMENCLATURE

a_T = reduction factor for relaxation times at temperature, T
 A = second approximation correction factor for calculation of Φ from G'
 B = second approximation correction factor for calculation of Φ from G''
 C = second approximation correction factor for calculation of Φ from η'
 G' = real part of the complex dynamic shear modulus
 G'' = imaginary part of the complex dynamic shear modulus
 G_i = contribution of i th mechanism to the instantaneous rigidity
 G'_{T_0} = G' reduced to temperature T_0
 G''_{T_0} = G'' reduced to temperature T_0
 k = constant in expression for Φ as a power function of τ
 m = negative slope of plot for $\log \Phi$ against $\log \tau$
 t = time
 T = absolute temperature
 T_0 = reference temperature (usually 298° K)
 σ = shear stress
 γ = shear strain
 $\dot{\gamma}$ = rate of shear strain
 Γ = gamma function
 η = steady flow viscosity
 η' = real part of the complex dynamic viscosity
 η'_{T_0} = η' reduced to temperature T_0
 ρ = density
 τ = relaxation time
 τ_i = relaxation time associated with G_i
 ω = circular frequency (2π times frequency)
 ω_{T_0} = ω reduced to temperature T_0
 Φ = distribution function of relaxation times in shear ($\Phi d \ln \tau$ is the differential contribution to rigidity associated with relaxation times whose natural logarithms lie between $\ln \tau$ and $\ln \tau + d \ln \tau$)

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CORRELATION OF DYNAMIC AND STATIC MEASUREMENTS ON RUBBERLIKE MATERIALS *

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One of the questions which has been much discussed in the field of the mechanical properties of rubberlike materials is the relation between the elastic moduli measured by static and by dynamic experimental methods. Some investigators have obtained results which indicated that the static and dynamic moduli were essentially equal, whereas other workers have obtained significant differences between the two moduli.

Theoretical developments in this field in recent years have provided a fundamental viewpoint from which such questions can be examined. In terms of this theory, the mechanical behavior of rubberlike materials can be regarded as arising from a combination of elastic and viscous behavior which can be represented by a so-called generalized Maxwell model, consisting of an infinite set of Maxwell units (spring and dashpot in series) connected in parallel. This type of model is characterized by a distribution function, $E(\tau)$, which is called the distribution of relaxation times and which specifies the contribution to the total "instantaneous" modulus (measured so quickly that no viscous flow can take place) that is associated with a relaxation time, τ . The term *distribution of relaxation times* is, therefore, not completely accurate, since $E(\tau)$ is really a distribution of partial modulus as a function of relaxation time.

Static elastic modulus can be measured either by applying a fixed strain or a fixed load to the rubber sample. The stress or elongation which is produced is more or less time-dependent, however, and the measured value of stress or elongation at some arbitrary time value is ordinarily taken as defining the static modulus. Since the static modulus measured at fixed strain is the one most easily described in terms of the generalized Maxwell model, static modulus will be defined by that type of experiment in the present paper. Since the stress in a rubber sample held at fixed strain is time-dependent, it is obvious that there is no unique *static modulus* value for a rubberlike material, but only an apparent modulus which is a function of time. The static modulus of a material in the most general sense is, therefore, given by the complete curve of stress *vs.* time at constant strain; this will be referred to as the *stress relaxation curve* of the material. This may be expressed in terms of the distribution of relaxation times¹:

$$\frac{f}{s_0}(t) = \int_0^{\infty} E(\tau) e^{-t/\tau} d\tau \quad (1)$$

where f is the stress, s_0 is the fixed strain, and t is the time elapsed since the sample was strained.

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Dynamic modulus is ordinarily measured by applying sinusoidal vibrations to the sample. The dynamic modulus is, like the static modulus, not a unique quantity, since it is a function of frequency in general, even though it may be fairly constant over certain ranges of logarithmic frequency, just as the static modulus may be fairly constant over certain ranges of the logarithmic time scale. The dynamic modulus, E_{dyn} , as a function of circular frequency ω may be expressed in terms of the distribution of relaxation times²:

$$E_{\text{dyn}}(\omega) = \int_0^{\infty} E(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d\tau \quad (2)$$

The dynamic modulus of a material is fully expressed, therefore, only by the complete curve of dynamic modulus *vs.* frequency. The question of comparing static and dynamic modulus thus becomes in a more general sense the question of comparing the stress relaxation and E_{dyn} *vs.* frequency curves.

Some rough conclusions can be drawn from the fact that curves of static modulus *vs.* time and dynamic modulus *vs.* vibration period (reciprocal of frequency in cycles per second) are to a crude approximation the same and that these curves must either remain level or decrease with increasing time (or vibration period). It is generally true, then, that the dynamic modulus is approximately equal to, or larger than, the static modulus, since the vibration period in the dynamic measurement is ordinarily significantly smaller than the time value at which the static modulus is measured. The difference between the dynamic and static modulus depends on the magnitude of the relaxation time distribution between the vibration period and time values in question.

The dynamic modulus is not the only quantity of interest in vibration experiments; the energy losses which occur during vibration, or mechanical energy which is dissipated into heat, is of great interest as well. This can also be interpreted on the basis of the generalized Maxwell model, and if the vibration behavior is described in terms of a complex dynamic modulus, the real part of the complex modulus is the E_{dyn} mentioned previously, while the imaginary part of the complex modulus, which is related to the energy losses, can be written as $\omega \eta_{\text{dyn}}$ where η_{dyn} is an effective viscosity coefficient that is a function of frequency. This latter quantity is related to the distribution of relaxation times by the expression²:

$$\omega \eta_{\text{dyn}}(\omega) = \int_0^{\infty} E(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} d\tau \quad (3)$$

As a rough qualitative generalization in this case, energy losses are greatest at reciprocal frequency values, where the distribution of relaxation times has the largest values; static and dynamic moduli also show the greatest change with logarithmic time and frequency, respectively, in these regions.

Vibration behavior can be represented by a simple Voigt mechanical model (spring and dashpot in parallel) with an inertial mass in series, at any given frequency. However, for a material with a distribution of relaxation times, the modulus of the spring and the viscosity of the dashpot are both functions of frequency and, in fact, are the E_{dyn} and η_{dyn} already given.

Thus, both static and dynamic mechanical behavior can be regarded as resulting from the nature of the relaxation time distribution of the material and can be correlated on this basis. However, in deriving quantitative relationships the exact solution of the equations involved is often very difficult, and approximate methods are desirable for use in such cases. The present paper is

concerned with an examination of approximate methods of this sort. Attempted correlations of static and dynamic mechanical data on the basis of these approximations are also discussed.

STATIC MODULUS

The distribution of relaxation times $E(\tau)$ can, in principle, be calculated from static modulus or relaxation of stress data by inversion of the integral in Equation 1. This can be done by use of the Laplace transform, but the procedure involved is too complicated to be conveniently usable in most cases. A simple approximate relation which has been proposed for use in this case is that the distribution of relaxation times in terms of logarithmic time, $E'(\log_{10} \tau)$, at any value of relaxation time τ , is equal to the negative slope of the relaxation curve plotted as f/s_0 vs. logarithmic time ($\log_{10} t$) at the same value of time τ . A prime is added to the symbol for the distribution function here to indicate that the logarithmic distribution is a different function from the linear distribution $E(\tau)$. The distribution of relaxation times in terms of logarithmic time is simply related to the distribution in terms of linear time:

$$E'(\log_{10} \tau) = 2.303 \tau E(\tau) \quad (4)$$

which follows from the fact that by definition:

$$E'(\log_{10} \tau) d \log_{10} \tau = E(\tau) d\tau \quad (5)$$

This is one case of the general relation for transforming distribution functions:

$$N(x) dx = \pm N'(y) dy \quad (6)$$

where N represents the distribution function and x and y are functions of some common parameter; the sign is chosen so that N is positive on both sides of the expression. Throughout the remainder of this paper, "log" will denote logarithms to the base 10 in all cases, and the subscript 10 will be dropped; natural logarithms will be denoted "ln".

This approximation can be derived in the following way. By substitution of Equation 5, Equation 1 may be rewritten as:

$$f/s_0(t) = \int_{-\infty}^{+\infty} E'(\log \tau) e^{-t/\tau} d \log \tau \quad (7)$$

The negative slope of the static modulus curve plotted vs. logarithmic time is then obtained by differentiation under the integral sign:

$$-\frac{d(f/s_0)}{d \log t} = \int_{-\infty}^{+\infty} E'(\log \tau) \left[\frac{2.303 t e^{-t/\tau}}{\tau} \right] d \log \tau \quad (8)$$

This expression is of the general form:

$$I = \int \phi E'(\log \tau) d \log \tau \quad (9)$$

where ϕ is the function in square brackets in Equation 8. This function specifies the intensity of the contribution of various regions of the relaxation time distribution, $E'(\log \tau)$, to the value of the integral, I , and therefore may be referred to as an intensity function. This function is plotted vs. $(\log \tau - \log t)$ in Figure 1; it has a fairly sharp peak at $\tau = t$ and drops off to zero on both sides

of the peak. The negative slope of the relaxation curve is therefore determined by the nature of the relaxation time distribution in the immediate neighborhood of the time value, t , at which the slope is measured. If the distribution function is a constant in this region, it can be taken from under the integral sign in Equation 8, and since the remaining integral has a value of unity:

$$\int_{-\infty}^{+\infty} \left[\frac{2.303t e^{-t/\tau}}{\tau} \right] d \log \tau = 1 \quad (10)$$

we obtain the desired relation:

$$-\frac{d(f/s_0)}{d \log t} = [E'(\log \tau)]_{\tau=t} \quad (11)$$

This relation may also be regarded as resulting from a replacement of the bracketed function in Equation 8 by a Dirac δ -function, $\delta(\tau - t)$, having a

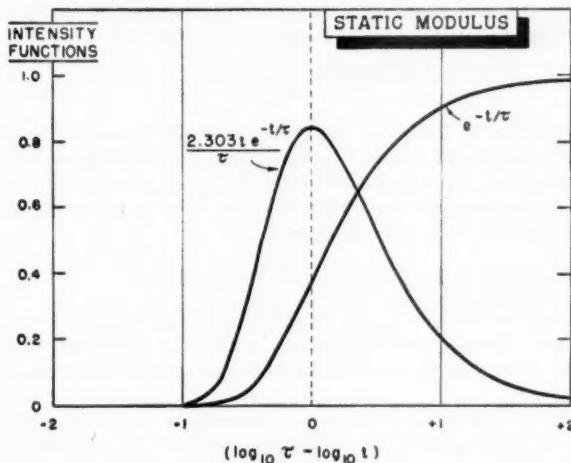


FIG. 1.—Intensity functions in integrals of Equations 7 and 8.

numerical value unity, and no assumption is necessary regarding the form of $E'(\log \tau)$; Equation 10 indicates that the *normalization factor* of the δ -function is unity in this case. This general approach has been used by ter Haar³. This relation can be arrived at by still another path, using a method adopted by Ferry⁴, in which Equation 7 is written in approximate form as:

$$f/s_0(t) = \int_{\log t}^{+\infty} E'(\log \tau) d \log \tau \quad (12)$$

This approximation represents a replacement of the intensity function, $e^{-t/\tau}$, in Equation 7 by a *cutoff function* which has a value of zero where $\log \tau$ is less than $\log t$ and a value of unity where $\log \tau$ is greater than $\log t$; the approximation that this involves can be seen by reference to the correct intensity function, which is shown in Figure 1. Then, by differentiating both sides of Equation 12 with respect to $\log t$, Equation 11 is immediately obtained.

Actually, the approximation given in Equation 11 is capable of much greater generalization. Dividing the left-hand side of Equation 11 by 2.303 t and the right-hand side by 2.303 τ , and utilizing Equation 4, one obtains after transformation:

$$-\frac{d(f/s_0)}{dt} = [E(\tau)]_{\tau=t} \quad (13)$$

Therefore the distribution of relaxation times in terms of linear τ is given approximately by the negative slope of the relaxation curve plotted *vs.* linear t . Then, considering any general function of τ or t , θ , and applying Equation 6 in the form:

$$\begin{aligned} E(\tau)d\tau &= \pm E[\theta(\tau)]d\theta(\tau) \\ &= \pm E[\theta(\tau)]\theta'(\tau)d\tau \end{aligned} \quad (14)$$

we may divide the left-hand side of Equation 13 by $\theta'(t)$ and the right-hand side by $\theta'(\tau)$, and this gives, after transformation, the completely general approximate relation:

$$E[\theta(\tau)] = \left[\frac{df/s_0}{d\theta(t)} \right]_{t=\tau} \quad (15)$$

The absolute value is taken on the right-hand side because the distribution function must always be positive, whereas the first derivative may be either positive or negative, depending on whether θ is a decreasing or increasing function of t . This relation can also be derived from Equation 11 even more directly by writing Equation 11 in the form:

$$-d(f/s_0) = E(\log t)d\log t \quad (16)$$

where the prime on the distribution function has been dropped for convenience. Equation 6 may then be applied directly to the right-hand side of this expression, letting $x = \log t$ and $y = \theta(t)$, and on rearrangement one obtains Equation 15.

Equation 11 is, therefore, simply one particular form of the general approximation expression (Equation 15), which represents an infinite family of similar approximation expressions. And since the various explicit forms of Equation 15, such as Equations 11 and 13, are all equivalent and mutually interconvertible, they can all be regarded as the "same" approximation and will all have the same intrinsic accuracy—that is, neglecting the possible variations in accuracy with which the different first derivatives could be measured in actual computations. This family of relations will be referred to as *first approximation expressions*.

In some cases, it may be desirable to use a more accurate expression than Equation 11. Such an expression can be obtained by considering the case where the distribution function, $E'(\log \tau)$, is not a constant, but is a linear function in $\log \tau$:

$$E'(\log \tau) = \alpha + \beta(\log \tau - \log t) \quad (17)$$

where α is the value of $E'(\log \tau)$ at $\tau = t$. Substituting this distribution into Equation 8:

$$-\frac{d(f/s_0)}{d\log t} = \alpha + 0.251 \beta \quad (18)$$

By differentiation of Equation 18 with respect to $\log t$ again, remembering that α is a function of t , and by use of Equation 17:

$$-\frac{d^2(f/s_0)}{d \log t^2} = \beta \quad (19)$$

This may, then be introduced for the value of β in Equation 18, and after rearrangement, the final result obtained is:

$$[E'(\log \tau)]_{\tau=t} = \alpha = -\frac{d(f/s_0)}{d \log t} + 0.251 \frac{d^2(f/s_0)}{d \log t^2} \quad (20)$$

This represents an improvement on Equation 11, in which a "second approximation" is obtained by addition of a correction term involving the second derivative of the relaxation curve. [An alternative second approximation expression can be derived by a method which is described in an accompanying article by Ferry, Fitzgerald, Grandine, and Williams⁵.]

The nature of the second approximation expression above is shown graphically in Figure 2. The intensity function in the integral of Equation 8, taken

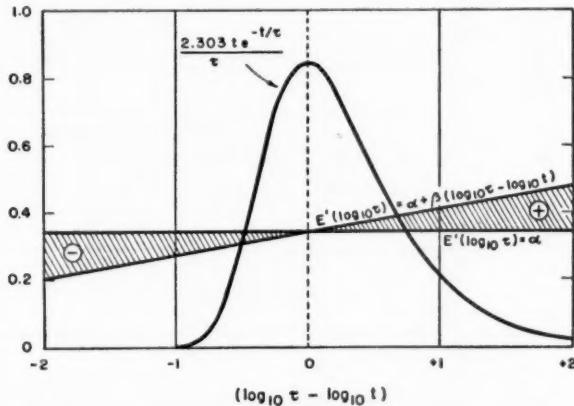


FIG. 2.—Graphical representation of derivation of second approximation, Equation 20.

from Figure 1, is shown, with the distribution functions where $E'(\log \tau)$ is a constant and a linear function of $\log \tau$. The difference between the two distribution functions is shown as a shaded region, and this shaded region, multiplied by the intensity function, corresponds to the added correction term in Equation 18 and in turn to the added correction term in Equation 20. This shaded region has opposite sign on opposite sides of $\log \tau = \log t$, and tends to partially compensate itself, but not completely. The graph shows a case for which β is positive. Equation 20 is exact and not an approximation when the distribution function is of the form of Equation 17.

The effect of the added correction term in Equation 20 was checked by calculating the distribution of relaxation times corresponding to an experimental stress-relaxation curve of polyisobutylene, by use of the first and second approximation Equations 11 and 20, and the results are shown in Figure 3. The relaxation curve used here is a previously unpublished curve obtained by

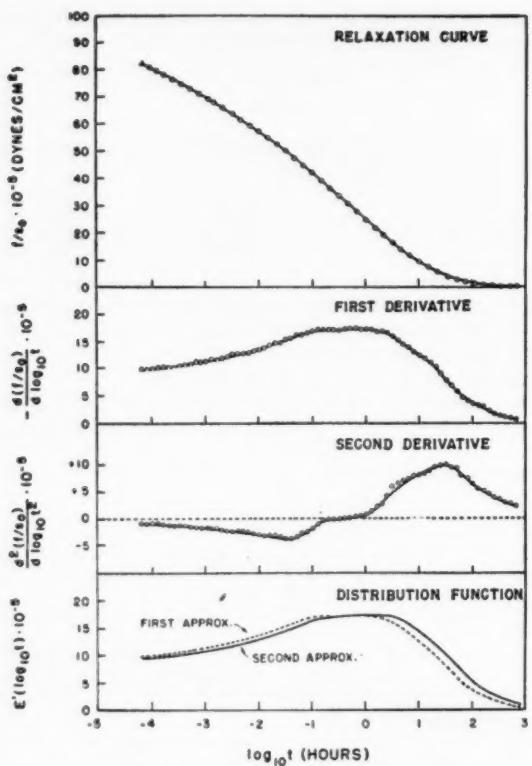


FIG. 3.—Calculation of first and second approximation distribution functions from static modulus (stress relaxation) curve of polyisobutylene at 25° C.

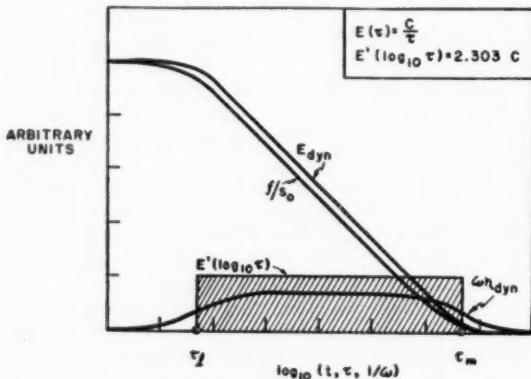


FIG. 4.—Static modulus, dynamic modulus, and dynamic loss functions corresponding to the distribution function in Equation 42a.

Andrews and Tobolsky for the standard polyisobutylene sample distributed by Marvin of the National Bureau of Standards⁶. The relaxation curve corresponds to 25° C, and the relaxation-time distributions calculated from it therefore refer to 25° C also. The first derivative was measured graphically from a magnified plot of the relaxation curve, and the second derivative was determined graphically from a magnified plot of the smoothed first derivative curve. The first approximation to the distribution function is the same as the first derivative, and the second approximation was calculated from the smoothed

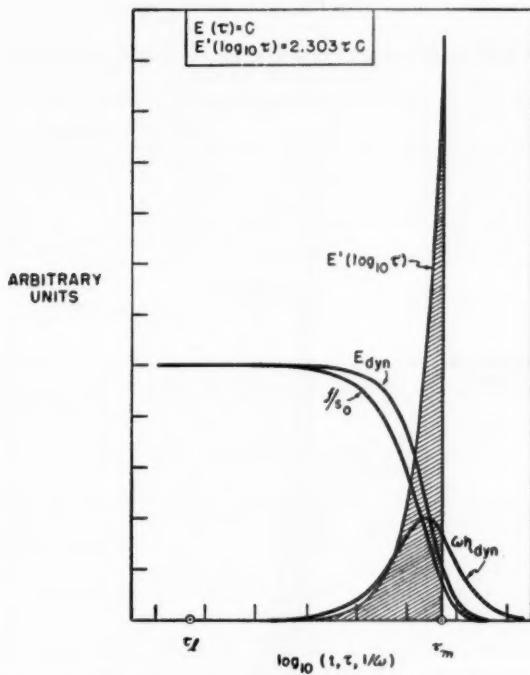


FIG. 5.—Static modulus, dynamic modulus, and dynamic loss functions corresponding to the distribution function in Equation 45a.

first and second derivative curves by use of Equation 20. The difference between the first and second approximation distribution functions is small, but nevertheless significant. It is also interesting in regard to the mechanical behavior of polyisobutylene that the distribution of relaxation times goes through a definite maximum in this region.

A somewhat different approximate method for calculating the distribution of relaxation times from the relaxation (static modulus) curve, which does not involve taking derivatives of the relaxation curve, has been proposed by ter Haar³. He expresses his distribution function in terms of *relaxation frequencies*, or reciprocal relaxation times, and in the symbolism of the present paper, the

approximation which he proposes is:

$$[E(1/\tau)]_{\tau=t} = t \cdot \frac{f}{s_0}(t) \quad (21)$$

In case there is a residual elastic stress which does not relax in the relaxation region under consideration, this must be subtracted from f/s_0 in this equation. This expression can be written in terms of the distribution function, $E'(\log \tau)$, by using Equation 6 to transform $E(1/\tau)$, and the result obtained is:

$$[E'(\log \tau)]_{\tau=t} = 2.303 \frac{f}{s_0}(t) \quad (22)$$

According to this relation, the distribution function, $E'(\log \tau)$, is a simple

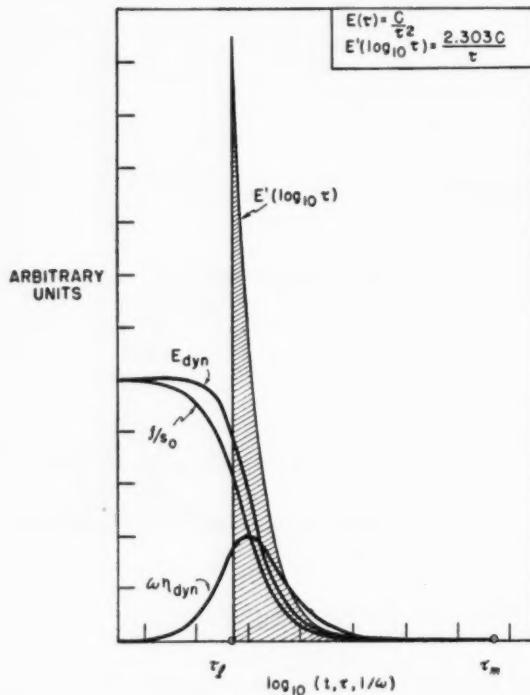


FIG. 6.—Static modulus, dynamic modulus, and dynamic loss functions corresponding to the distribution function in Equation 47a.

multiple (by a factor 2.303) of the relaxation curve, when $\log \tau$ and $\log t$ are plotted on the same scale.

Comparison of the relaxation curve and approximate relaxation time distributions for polyisobutylene given in Figure 3 shows that the relation (Equation 22) does not hold in this particular case. Plots of the distribution function and corresponding relaxation curve (f/s_0) for three widely different forms of $E'(\log \tau)$ are given in Figures 4, 5, and 6. (These graphs are discussed in more

detail in a later section.) Figures 4 and 5 show that Equation 22 does not hold for relaxation-time distributions of this form, either, even as a rough approximation. In fact, for the distribution of Figure 5, the distribution function increases sharply, while the relaxation curve decreases sharply. However, for the distribution shown in Figure 6, ter Haar's approximation, in the form of Equation 22, is found to hold exactly for all time values well within the lower and upper limits, τ_l and τ_m , at which the distribution function is arbitrarily cut off. The distribution denoted here as $E(1/\tau)$ is symbolized by $N(\nu)$ in ter Haar's publications, and the distribution represented in Figure 6 when written in that form corresponds to:

$$E(1/\tau) \equiv N(\nu) = \text{const.} \quad (23)$$

between the limits of the distribution and to zero outside those limits. The distributions used by ter Haar in checking the accuracy of his approximation were in many cases of this form. The results obtained here indicate that the accuracy would be best in those cases. The behavior observed in Figures 3, 4, and 5 shows that Equation 22 is much more restricted in its range of application than the approximation (Equation 11 or 15) which involves the first derivative. This latter approximation is referred to by ter Haar as the "Alfrey approximation", and the form of this approximation which he uses to calculate $N(\nu)$ or $E(1/\tau)$ can be readily derived from Equation 15 by setting $\theta(\tau) = 1/\tau$ and $\theta(t) = 1/t$:

$$N(\nu) \equiv E(1/\tau) = \left| \frac{d(f/s_0)}{d(1/t)} \right| = -t^2 \frac{d(f/s_0)}{dt} \quad (24)$$

The negative sign is retained in the final expression, since the derivative will always be negative, and the use of this negative sign is, therefore, equivalent to taking the absolute value.

DYNAMIC MODULUS AND LOSS

The dynamic modulus is related to the distribution of relaxation times as given in Equation 2. This relation may be rewritten, by substitution of Equation 5, in the form:

$$E_{\text{dyn}}(\omega) = \int_{-\infty}^{+\infty} E'(\log \tau) \left[\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \right] d \log \tau \quad (25)$$

This integral is again of the form of Equation 9, and the *intensity function* in square brackets is shown plotted *vs.* $(\log \tau - \log 1/\omega)$ in Figure 7. The distribution of relaxation times can be calculated approximately from the curve of dynamic modulus *vs.* $\log 1/\omega$ by use of the relation:

$$[E'(\log \tau)]_{\tau=1/\omega} = - \frac{d E_{\text{dyn}}}{d \log 1/\omega} \quad (26)$$

in which the distribution function is taken to be equal to the negative slope of the dynamic modulus curve. This approximation is the analog of Equation 11 for static modulus data, and as in that case is simply one member of an infinite family of equivalent expressions of the general form:

$$E[\theta(\tau)] = \left| \frac{d E_{\text{dyn}}}{d \theta(1/\omega)} \right|_{1/\omega=\tau} \quad (27)$$

which is the dynamic modulus analog of Equation 15.

Equation 26 can be derived by the same general methods that were used in deriving Equation 11 in the static modulus case. The general expression for the negative slope of the curve of E_{dyn} vs. $\log(1/\omega)$ can be obtained by differentiating Equation 25 under the integral sign, giving the (exact) relation:

$$-\frac{d E_{\text{dyn}}}{d \log 1/\omega} = \int_{-\infty}^{+\infty} E'(\log \tau) \left[\frac{4.606 \omega^2 \tau^2}{(1 + \omega^2 \tau^2)^2} \right] d \log \tau \quad (28)$$

The intensity function in square brackets is plotted in Figure 7 and has a fairly sharp peak, indicating that the slope of the dynamic modulus curve is determined by the nature of the relaxation time distribution in the immediate neighborhood of the value $\log 1/\omega$ at which the slope is measured. If $E'(\log \tau)$ can be assumed to be constant in the neighborhood of $\tau = 1/\omega$, the distribution function may be brought out from under the integral sign, and since the remain-

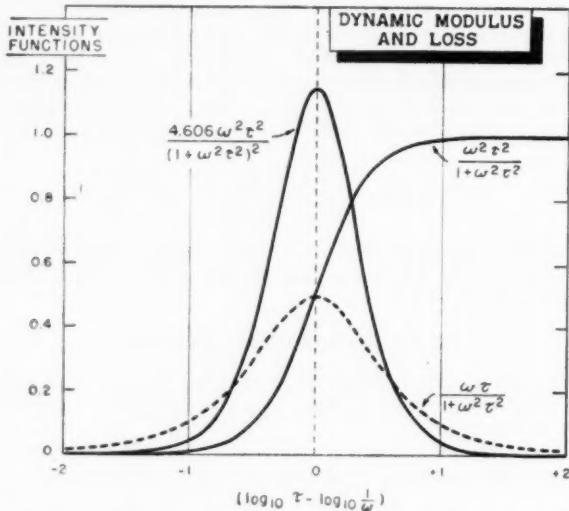


FIG. 7.—Intensity functions in integrals of Equations 25, 28, and 35. Solid curves refer to dynamic modulus; dashed curve to dynamic loss.

ing integral is equal to unity:

$$\int_{-\infty}^{+\infty} \left[\frac{4.606 \omega^2 \tau^2}{(1 + \omega^2 \tau^2)^2} \right] d \log \tau = 1 \quad (29)$$

one immediately obtains the desired relation, given in Equation 26. As in the static modulus case, this relation can also be obtained by replacing the intensity function in Equation 28 by a Dirac δ -function, or by replacing the intensity function in Equation 25 by a cutoff function⁴:

$$E_{\text{dyn}}(\omega) = \int_{\log 1/\omega}^{+\infty} E'(\log \tau) d \log \tau \quad (30)$$

followed by differentiation of both sides of the equation with respect to $\log 1/\omega$.

In order to obtain a second-order approximation of improved accuracy, we may substitute a distribution of the form:

$$E'(\log \tau) = \alpha + \beta (\log \tau - \log 1/\omega) \quad (31)$$

into Equation 28. However, because the intensity function in Equation 28 is symmetrical around its peak at $\log \tau = \log 1/\omega$, it is evident that the contribution of the second term in Equation 31 to the value of the slope is zero. Referring to Figure 2, the positive and negative contributions to the slope which result when the shaded areas are multiplied by the intensity function of Equation 28 in this case exactly compensate each other. Thus Equation 26 represents a second-order approximation as well as a first-order approximation. Computation of $E'(\log \tau)$ from the slope of the dynamic modulus curve by use of Equation 26 is, therefore, a more accurate method than computation from the slope of the static modulus curve from the analogous Equation 11. It is evident, in addition, that if $E'(\log \tau)$ is expanded in a power series in $(\log \tau - \log 1/\omega)$, the contribution of all odd power terms to the slope is zero, as a result of the symmetry of the intensity function in Equation 28.

An approximate relation by which the distribution of relaxation times can be computed without taking derivatives has been proposed by ter Haar³ for dynamic modulus data also. He presents this relation in terms of a distribution function $N(\omega) = [N(\nu)]_{\nu=\omega}$, but his expression may be written in our symbolism as:

$$[E(1/\tau)]_{1/\tau=\omega} \propto \frac{E_{\text{dyn}}(\omega)}{\omega} \quad (32)$$

This represents a proportionality rather than an equality. If the distribution function $E(1/\tau)$ is transformed to $E'(\log \tau)$ by use of Equation 6, this relation takes the form:

$$[E'(\log \tau)]_{\tau=1/\omega} \propto 2.303 E_{\text{dyn}}(\omega) \quad (33)$$

This is very similar to Equation 22 for static modulus data except that this expression involves a proportionality rather than an equality. According to this relation, the distribution function, $E'(\log \tau)$, should be directly proportional to the dynamic modulus. As in Equation 22, Relation 33 clearly does not hold for relaxation time distributions of the forms shown in Figures 4 and 5; however, Equation 33 does hold exactly for the distribution represented in Figure 6. Examination of the characteristics of the dynamic modulus function in Figure 6 indicates that the proportionality constant involved in Relation 33 is $2/\pi$, and when the right-hand side is multiplied by this factor we obtain the equality:

$$[E'(\log \tau)]_{\tau=1/\omega} = \frac{4.606}{\pi} E_{\text{dyn}}(\omega) \quad (34)$$

The range of applicability of this equation is about the same as that of Equation 22, which is narrower than that of the relation involving the first derivative given as Equation 27.

The energy loss term for sinusoidal vibrations has been given in Equation 3. This may be written in terms of the logarithmic distribution of relaxation times by substitution of Equation 5, giving:

$$\omega \eta_{\text{dyn}}(\omega) = \int_{-\infty}^{+\infty} E'(\log \tau) \left[\frac{\omega \tau}{1 + \omega^2 \tau^2} \right] d \log \tau \quad (35)$$

A plot of the intensity function in this integral, in the form of a dashed curve, is shown in Figure 7. It is a symmetrical curve around its peak at $\log \tau = \log 1/\omega$, as is the intensity function for the slope of the dynamic modulus curve in Equation 28. It is therefore not necessary to differentiate this expression in order to obtain a peaked intensity curve, as was true for the static and dynamic modulus in Equations 7 and 25. The peak in this curve is not quite so sharp as that of the intensity curve in Equation 28, but the value of $\omega\eta_{dyn}$ is still determined by the nature of $E'(\log \tau)$ in the immediate neighborhood of $\log \tau = \log 1/\omega$. This curve is essentially the square root of the intensity curve in Equation 28.

Approximate expressions for $\omega\eta_{dyn}$ may be derived in the same manner as previously. If $E'(\log \tau) = \text{const.}$ is substituted into Equation 35, and brought out from under the integral sign, the remaining integral has the value $\frac{\pi}{4.606}$:

$$\int_{-\infty}^{+\infty} \left[\frac{\omega\tau}{1 + \omega^2\tau^2} \right] d\log \tau = \frac{\pi}{4.606} \quad (36)$$

and one obtains the first-order approximation that:

$$\omega\eta_{dyn}(\omega) = \frac{\pi}{4.606} [E'(\log \tau)]_{\tau=1/\omega} \quad (37)$$

This expression can also be obtained by substitution of $\frac{\pi}{4.606} \delta(\tau - 1/\omega)$ for the intensity function in Equation 35. According to Equation 37, the distribution function, $E'(\log \tau)$, is proportional to the quantity $\omega\eta_{dyn}$. Dynamic viscosity can also be represented by use of a cutoff function⁴:

$$\eta_{dyn} = \int_{-\infty}^{\log 1/a\omega} \tau E'(\log \tau) d\log \tau \quad (38)$$

where a is a constant with a value in the neighborhood of unity, and by differentiation of both sides of this equation one obtains the additional approximation that:

$$[E'(\log \tau)]_{\tau=1/\omega} = -a\omega \frac{d\eta_{dyn}}{d\log \omega} \quad (39)$$

From the symmetry of the intensity function in Equation 35, it can be concluded that Equation 37 also represents the second-order approximation of this type, since the contribution to $\omega\eta_{dyn}$ from the second term in Equation 31 is zero. Similarly, the contribution from all odd power terms in a generalized expansion of the form of Equation 31 is zero, as in the case of the slope of the dynamic modulus curve.

To relate dynamic loss and relaxation time distribution without taking derivatives, ter Haar³ has proposed the following relation, which, when written in the author's symbolism, is:

$$\omega\eta_{dyn}(\omega) \propto \omega [E(1/\tau)]_{1/\tau=\omega} \quad (40)$$

where a proportionality rather than an equality is specified. If $E(1/\tau)$ is transformed to $E'(\log \tau)$, this expression assumes the form:

$$\omega\eta_{dyn}(\omega) \propto \frac{1}{2.303} [E'(\log \tau)]_{\tau=1/\omega} \quad (41)$$

This is essentially the same relation as in Equation 37 and becomes identical with 37 if the right-hand side is multiplied by a proportionality constant of $\pi/2$ and the proportionality is changed to an equality. This relation therefore requires no separate discussion. It is of interest to note, however, that, unlike the other two relations proposed by ter Haar, this relation holds essentially for a relaxation-time distribution of the form shown in Figure 4, and less satisfactorily for the distributions in Figures 5 and 6.

PROTOTYPE DISTRIBUTION FUNCTIONS

As an alternative to mathematical analysis of the structure of the integrals involved, the problem of deriving approximate relations may be approached by studying the behavior of certain particular forms of relaxation time distribution. One type of distribution which has been found particularly useful in this connection⁷ is a "logarithmic box" distribution, which is a constant in terms of $\log \tau$ between a lower and upper limit τ_l and τ_m and zero outside those limits:

$$\begin{aligned} E'(\log \tau) &= 2.303C(\tau_l < \tau < \tau_m) \\ &= 0(\tau < \tau_l, \tau > \tau_m) \end{aligned} \quad (42a)$$

This corresponds to a distribution in linear τ of the form:

$$\begin{aligned} E(\tau) &= C/\tau(\tau_l < \tau < \tau_m) \\ &= 0(\tau < \tau_l, \tau > \tau_m) \end{aligned} \quad (42b)$$

The static modulus, dynamic modulus, and dynamic-loss functions corresponding to this distribution can be obtained by substitution of Equation 42b into Equations 1, 2, and 3:

$$f/s_0 = C[Ei(-t/\tau_l) - Ei(-t/\tau_m)] \quad (43a)$$

$$E_{\text{dyn}} = \frac{C}{2} \ln \frac{1 + \omega^2 \tau_m^2}{1 + \omega^2 \tau_l^2} \quad (43b)$$

$$\omega\eta_{\text{dyn}} = C[\tan^{-1}\omega\tau_m - \tan^{-1}\omega\tau_l] \quad (43c)$$

These three functions are shown plotted, together with the distribution function itself, for a distribution which is five log cycles in width, in Figure 4. For the time, or reciprocal frequency range which lies well within the limits of the distribution function, the static and dynamic modulus curves are straight lines, with slope equal to the height of the distribution function, $E'(\log \tau)$, and the height of the dynamic loss curve is approximately constant and equal to $\pi/4.606$ times the height of the distribution curve. This particular relaxation time distribution therefore leads to the first-order approximations, Equations 11, 26, and 37, which hold exactly for this distribution; it is essentially equivalent to the substitution of $E'(\log \tau) = \text{const.}$ into the various integrals involved. The general Equations 15 and 27 also hold exactly for this distribution.

Another useful relation, between static and dynamic modulus, can be obtained from this distribution. In the intermediate range, the static and dynamic modulus curves are identical except for a slight lateral shift. The amount of this shift is given by the relation that the time value, t , in the static modulus curve corresponding to any arbitrary value of modulus is related to the reciprocal frequency $1/\omega$ at which dynamic modulus has the same value by the

expression:

$$t = \frac{0.561}{\omega} \quad (44)$$

Using this relationship, the static and dynamic modulus curves can be related directly, without going through the intermediate step of calculating the distribution of relaxation times.

It is, therefore, of interest to see how generally this relationship holds, and this can be checked by examining the behavior of the two relaxation-time distributions shown in Figures 5 and 6, which differ considerably from Equation 42a and in opposite directions. The distribution shown in Figure 5 is of the form:

$$\begin{aligned} E'(\log \tau) &= 2.303C\tau(\tau_l < \tau < \tau_m) \\ &= 0(\tau < \tau_l, \tau > \tau_m) \end{aligned} \quad (45a)$$

This corresponds to a linear distribution of the form:

$$\begin{aligned} E(\tau) &= C(\tau_l < \tau < \tau_m) \\ &= 0(\tau < \tau_l, \tau > \tau_m) \end{aligned} \quad (45b)$$

If one divides Equation 45a by the constant, τ_m , representing the upper limit of the distribution, one obtains the modified form:

$$\begin{aligned} E'(\log \tau) &= \frac{2.303C\tau}{\tau_m} (\tau_l < \tau < \tau_m) \\ &= 0(\tau < \tau_l, \tau > \tau_m) \end{aligned} \quad (45c)$$

which is more convenient in that it is independent of position along the logarithmic τ scale, for a given value of C . The corresponding linear distribution is obtained by dividing Equation 45b by τ_m . The static modulus, dynamic modulus, and dynamic loss functions corresponding to this distribution in its modified form are:

$$f/s_0 = C \left\{ \left[e^{-t/\tau_m} - \frac{\tau_l}{\tau_m} e^{-t/\tau_l} \right] - \frac{t}{\tau_m} [Ei(-t/\tau_l) - Ei(-t/\tau_m)] \right\} \quad (46a)$$

$$E_{\text{dyn}} = C(1 - \tau_l/\tau_m) - \frac{C}{\omega\tau_m} (\tan^{-1}\omega\tau_m - \tan^{-1}\omega\tau_l) \quad (46b)$$

$$\omega\eta_{\text{dyn}} = \frac{C}{2\omega\tau_m} \ln \frac{1 + \omega^2\tau_m^2}{1 + \omega^2\tau_l^2} \quad (46c)$$

For distributions where $\tau_l \ll \tau_m$, the second term in the first square brackets of Equation 46a and the second term in the first parentheses of Equation 46b are essentially zero and may be dropped. These functions are plotted, again for the case where τ_l and τ_m differ by five logarithmic cycles, in Figure 5.

The distribution in Figure 6 is of the form:

$$\begin{aligned} E'(\log \tau) &= \frac{2.303C}{\tau} (\tau_l < \tau < \tau_m) \\ &= 0(\tau < \tau_l, \tau > \tau_m) \end{aligned} \quad (47a)$$

which may also be written as a linear distribution:

$$\begin{aligned} E(\tau) &= C/\tau^2 (\tau_l < \tau < \tau_m) \\ &= 0 (\tau < \tau_l, \tau > \tau_m) \end{aligned} \quad (47b)$$

Multiplying Equation 47a by τ_m gives the more convenient form

$$\begin{aligned} E'(\log \tau) &= \frac{2.303C\tau_m}{\tau} (\tau_l < \tau < \tau_m) \\ &= 0 (\tau < \tau_l, \tau > \tau_m) \end{aligned} \quad (47c)$$

This modified form again has the advantage that it is independent of position along the logarithmic τ scale, for a given value of C . The corresponding linear distribution is obtained by multiplying Equation 47b by τ_m .

The static and dynamic functions corresponding to this modified distribution are:

$$f/s_0 = \frac{C\tau_m}{t} [e^{-t/\tau_m} - e^{-t/\tau_l}] \quad (48a)$$

$$E_{\text{dyn}} = C\tau_m \omega (\tan^{-1}\omega\tau_m - \tan^{-1}\omega\tau_l) \quad (48b)$$

$$\omega\eta_{\text{dyn}} = \frac{C\tau_m \omega}{2} \ln \left[\frac{1 + (\tau_l \omega)^2}{(\tau_l/\tau_m)^2 + (\tau_l \omega)^2} \right] \quad (48c)$$

If $\tau_l \ll \tau_m$, the first term in the denominator of the bracketed expression in Equation 48c is effectively zero and can be dropped. The curves of these functions shown in Figure 6 are for a distribution extending over five logarithmic cycles of τ .

Returning to the question of the relation between static and dynamic modulus, the simple lateral shift relation between static and dynamic modulus curves which was observed for the distribution shown in Figure 4 no longer holds for the distributions shown in Figures 5 and 6. However, the dynamic modulus curve still lies to the right of the static modulus curve in all cases, and from inspection of the curves it appears that the lateral distance between the curves at a given modulus value is greater where the second derivative of the curves is negative and less where the second derivative is positive. This suggests that a second-order approximation to Equation 44 might be obtained by addition of a second term involving the second derivative of one of these curves.

This was checked for the Distribution 45a shown in Figure 5 by measuring the second derivatives of the static and dynamic modulus curves graphically, at different modulus values, and comparing these with the displacement of the two curves at the modulus value in question. The results are shown in Figure 8. It would be hoped that the displacement was the same as in Figure 4 (which is $\log 1.781$ or $-\log 0.561$) where the second derivative was zero, with some simple relationship to the second derivative for nonzero values. Examination of Figure 8 shows that neither of these hopes is realized. Where the curves in Figure 8 show a fairly linear section, this corresponds to such a small region of the modulus curves that this furnishes no useful relation. A similar behavior would probably be found for Distribution 47a. Thus, this approach does not seem to lead to a useful second approximation for Equation 44. However, Distributions 45a and 47a are both fairly extreme in shape, and for distributions which are obtained in practice, which are probably closer to the form of 42a, Equation 44 should be a fairly satisfactory approximation.

It was noted previously that the first approximation expressions (Equations 11, 26, and 37) hold exactly for a distribution of the form of Equation 42a which is illustrated in Figure 4 (provided that one remains well within the limits of the distribution function). However, Equations 11 and 26 also hold exactly for the Distribution 47a which is shown in Figure 6; and this is of course true also for these equations in their generalized forms (15 and 27). It was men-

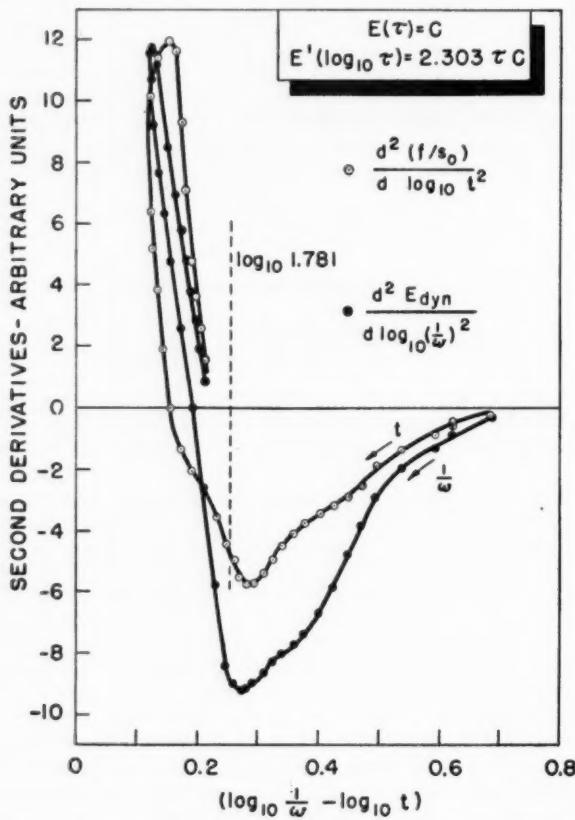


Fig. 8.—Relation between second derivatives of static and dynamic modulus curves and horizontal displacement of curves for distribution 45a shown in Figure 5. Arrows by curves indicate direction of increasing time and reciprocal frequency; dashed line indicates displacement corresponding to distribution (Equation 42a) shown in Figure 4.

tioned in addition that ter Haar's approximations (Equations 22 and 34) hold exactly for the Distribution 47a. The fact that $E'(\log \tau)$ can be exactly proportional to the modulus value and also to the slope of the modulus curve simultaneously, in both the static and dynamic cases, for this distribution, is explained by the fact that the distribution function, static modulus, and dynamic modulus curves are all decreasing exponential curves (in the region well within the limits of the distribution), when plotted as in Figure 6, and for such

curves the slope is equal to the function value (except for a multiplying constant). For the dynamic loss factor, ter Haar's approximation (Equation 41) holds exactly for Distribution 42a but not for Distribution 47a. Ferry's approximation (Equation 39) holds exactly for both Distribution 42a and 47a; the constant a has the values $2/\pi$ and unity in the two cases, respectively. The intensity function in the integral of Equation 39 (when the derivative is written out in explicit form) is not shown in Figure 7.

EXPERIMENTAL INVESTIGATIONS

In the previous sections of this paper, a number of approximate relations between static and dynamic mechanical quantities and the distribution of relaxation times have been given, as well as relations between these quantities themselves. The experimental data available for checking these relationships are not very extensive. However, some work has been done in this direction, and will be mentioned here. In all these cases, only the first-order approximations were used, and in particular the first-order approximations derived from the logarithmic box distribution (Equation 42a).

TABLE I

COMPARISON OF OBSERVED DYNAMIC LOSS WITH VALUES CALCULATED FROM CREEP CURVES FOR VULCANIZED NATURAL RUBBER⁸
(Vibration period = 20 seconds)

Sample	Type of creep curve	$\eta_{dyn} \times 10^{-4}$ (calcd.)	$\eta_{dyn} \times 10^{-4}$ (observed)
I	Tension	3.7	3.9
II	Tension	2.70	2.75
III	Tension	2.47	2.55
	Torsion	2.55	2.55

Kuhn and Künzle⁸ in 1947 attempted to correlate creep data and free torsional vibration data on three samples cut from a sheet of vulcanized natural rubber. They showed that for a material with a creep curve which is linear in logarithmic time:

$$\frac{\alpha - 1}{\sigma} = \frac{a + \ln t}{b} \quad (49)$$

where α is fractional elongation, σ is stress, and a and b are constants, the dynamic loss is given approximately by the expression:

$$\nu \eta_{dyn} = \frac{1}{12} \frac{b}{a^2} \quad (50)$$

where ν is vibration frequency in cycles per second. Their calculations of dynamic loss are shown in Table I with the experimentally determined values. Good agreement is obtained. Dynamic modulus could also be calculated successfully from creep data, provided that creep was also measured in torsion.

Similar calculations of dynamic loss for various vulcanized rubbers from static modulus data have been carried out by Dunell and Tobolsky⁹, essentially using Equations 11 and 37. Typical results are given in Table II, where E^0 is the slope of the relaxation curve plotted as static modulus *vs.* $\log t$. In general, experimental values are higher than calculated values by a factor of 2 to 10. However, the time range of the relaxation measurements did not overlap with

TABLE II

COMPARISON OF OBSERVED DYNAMIC LOSS WITH VALUES CALCULATED FROM STRESS RELAXATION DATA FOR VARIOUS RUBBER STOCKS⁹

Stock	Temp. (° C.)	E^0 (dynes/sq. cm. $\times 10^{-4}$)	$\omega_{dyn} \times 10^{-3}$ (calcd.)	$\omega_{dyn} \times 10^{-3}$ (observed)
Hevea gum	40	0.11	0.026	0.24
	100	0.20	0.045	0.13
Hevea tread	40	2.1	0.48	2.5
	100	2.5	0.55	1.1
GR-S gum	40	0.47	0.11	0.82
	100	0.47	0.11	0.42
Neoprene-GN gum	40	1.5	0.33	0.85
	100	1.5	0.33	0.68

the range of reciprocal frequency of the vibration measurements, and the relaxation data had to be extrapolated. This is probably the source of the discrepancies obtained here. Calculations of this sort for various textile materials gave generally better agreement. Values of dynamic loss calculated by these authors from creep data using the method of Kuhn and Künzle also tended to be somewhat lower than the experimental values, but the same difficulties of extrapolation were present in these calculations.

Lethersich¹⁰ has recently attempted to calculate dynamic viscosity from creep data for various plastic materials, using these same methods (or approximations). His results are given in Table III, where b is the slope of the creep curve *vs.* $\log t$, and G is dynamic modulus. Generally satisfactory agreement was obtained. The last two columns of this table actually represent $\nu\eta_{dyn}$ as well as η_{dyn} , since $\nu = 1$ here.

As a final example, a comparison is possible between some shear vibration data on a polyisobutylene sample at 25° C by Marvin, Fitzgerald, and Ferry¹¹, and static modulus data on a polymer of the same molecular weight by Andrews, Holmes, and Tobolsky¹². In this case also, the time ranges of the static modulus measurements did not overlap with that of the vibration measurements. However, relaxation of stress curves were measured at different temperatures, and other studies¹³ have indicated that curves at different temperatures can be superposed on one another by horizontal shift along the $\log t$ scale when reduced modulus (modulus multiplied by $298/T$) is plotted as ordinate; reduced modulus is identical with actual modulus at 25° C. A composite static modulus curve for 25° C extending into the time range of the vibration experiments was constructed in this way and is shown as a solid curve in Figure 9. Static modulus, f/s_0 , was measured in tension and has been converted to shear units by

TABLE III

COMPARISON OF OBSERVED DYNAMIC VISCOSITY IN TORSION WITH VALUES CALCULATED FROM CREEP DATA FOR VARIOUS PLASTIC MATERIALS¹⁰

Material	$b \times 10^{12}$	$G \times 10^6$	$\eta_{dyn} \times 10^7$ at 1 Cycle/second	
			Calcd.	Observed
Polyethylene	220	1.1	2.9	2.0
Polymethyl methacrylate	9.8	13.3	18.7	15.0
Ebonite	2.25	9.0	2.0	1.8
Polystyrene	2.5	12.0	3.9	2.5

multiplying by $\frac{1}{3}$. The position on the curve at which measurements could first be made at 25° C is indicated by an arrow. The part of the curve in the region of the vibration data was measured at -50° C. Experimental values of dynamic shear modulus are shown as circles and are plotted *vs.* $\log 0.561/\omega$ as abscissa, as indicated by Equation 44. The solid curve and experimental points show similar behavior—a marked rise in the same region. However, the agreement between static and dynamic modulus values is not so good as one would expect from Figures 4, 5, and 6, and further work would be desirable to investigate the reasons for this discrepancy. Perhaps the composite static modulus curve is not really identical with the curve that one would obtain if the whole curve were measured directly at 25° C.

In general, it can be said that the experimental work done so far seems to confirm the correctness of the general theory described here and the usefulness of approximate relations derived from it. Where discrepancies are observed,

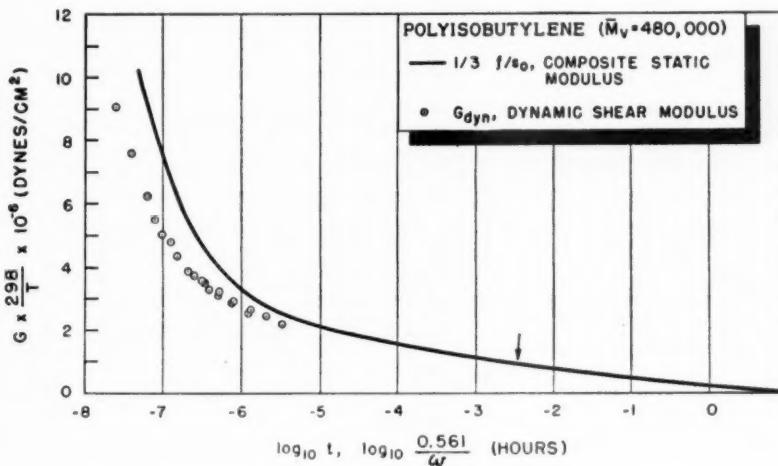


FIG. 9.—Comparison of static and dynamic shear modulus data on polyisobutylene at 25° C. Plotted as indicated by Equation 44.

reasonable causes for these discrepancies readily suggest themselves. Further experimental work is needed to check various aspects of this theory and to extend the range of direct experimental knowledge in this field.

SUMMARY

Dynamic and static measurements of rubberlike materials can be related in terms of a generalized Maxwell model which is assumed to represent the mechanical behavior of the system, the individual characteristics of the system being expressed by the nature of the relaxation time distribution of the model.

Such properties as dynamic modulus and dynamic viscosity measured in experiments involving sinusoidal vibrations and static modulus measured in experiments of relaxation of stress at constant strain can be expressed by integrals involving the distribution of relaxation times. The distribution of re-

laxation times can, therefore, be calculated from experimental data of this sort by suitable mathematical methods.

Because of the complexity of such calculations when carried out rigorously, the use of approximate methods is often desirable. A number of useful approximate relations can be derived by investigation of the mathematical structure of the integrals relating the distribution of relaxation times to the observed properties and by examination of the behavior of certain particular relaxation time distributions. Attempts to correlate dynamic and static data on the basis of this general theory by use of the approximate relations discussed have been reasonably successful.

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ELASTOVISCOSUS PROPERTIES OF AMORPHOUS POLYMERS IN THE TRANSITION REGION. I.*

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INTRODUCTION

It has been shown previously that for a given amorphous polymer, the stress relaxation curves determined at different temperatures may be made to coincide by a translation along the logarithmic time axis¹. This makes possible the construction of a composite stress relaxation curve or "master curve", valid over an extended time scale at any given temperature. The master curve can be conveniently plotted in the form of $\log E_{r,T_0}(t)$ vs. $\log(t)$, where $E_{r,T_0}(t)$, the relaxation modulus at a temperature T_0 , is the stress per unit strain in a sample maintained at a constant small strain for a time, t . When plotted in this form, a master curve for a given polymer is also valid at any other temperature by simply shifting the origin of the log time axis.

From the master curve $E_{r,T_0}(t)$ and from the amount of shift of the log time scale at each temperature, a new function $Q(t/K)$ may be defined as:

$$E_{r,T_0}(t) = Q(t/K) \quad (1)$$

In Equation (1), K is a function of temperature alone, which will be more explicitly defined subsequently, and t has the same numerical value on both sides of the equation. The function $Q(t/K)$ is a universal function of t/K which is valid at all temperatures, and may, therefore, be called the universal master relaxation curve for a given polymer.

An analytical or graphical representation of $Q(t/K)$, together with an analytical expression or tabulation of K as a function of T , are a complete representation of the viscoelastic properties of an amorphous polymer at all times and temperatures in the range of strains where the Boltzmann superposition principle applies. They can be used in principle to calculate any other property, such as dynamic modulus.

In a previous paper it was shown that the viscoelastic behavior of amorphous polymers can be classified into three distinct regions: a glassy region ($E_{r,T}(t) \sim 10^{10.5}$ dynes/cm.²) where the mechanical properties depend on previous thermal history, a transition region where the relaxation modulus lies approximately between 10^7 dynes/cm.² and $10^{10.5}$ dynes/cm.² and is independent of thermal history and of the molecular weight of the polymer, and a rubbery region where the relaxation modulus is less than 10^7 to $10^{7.5}$ dynes/cm.² and depends on the molecular weight of the polymer and on the presence or absence of cross-links².

In this paper new experimental data for $E_{r,T}(t)$ of a GR-S gum vulcanizate at a series of temperatures in the transition region are presented. The GR-S vulcanizate used is identical with that used and previously described¹. A

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master curve is constructed, an analytical formulation of $Q(t/K)$ is given, and the K values at different temperatures are tabulated. The results are compared with those previously obtained for polymethyl methacrylate, and striking similarities between the behavior of these two apparently very different polymers are discussed.

EXPERIMENTAL RESULTS FOR A GR-S GUM VULCANIZATE

The apparatus used in this investigation was a modification of the instrument described by McLoughlin². Stress was measured by means of a Schaevitz differential transformer mounted on a spring dynamometer; the transformer output was fed into a Brown Electronik recording potentiometer. Temperatures in the range between -33° and -64° C were maintained to an accuracy of 0.1-0.2° C. The accuracy of the measured absolute moduli was primarily

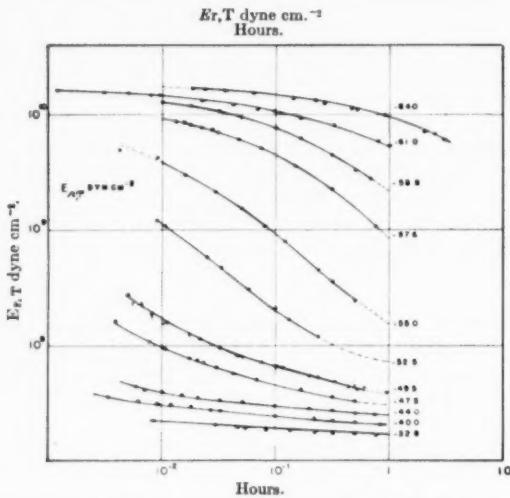


FIG. 1.— $\log E_{r,T}(t)$ vs. $\log (t)$ for GR-S gum stock.

determined by the temperature control, and was approximately 10 per cent. This accuracy was satisfactory considering the tremendous variation of modulus with temperature. In order to keep the stress in an easily measured range, the constant strain applied at different temperatures was varied between 0.3 and 18 per cent according to the initial value of the modulus.

Figure 1 shows the stress-relaxation curves at various temperatures, plotted as $\log E_{r,T}(t)$ vs. $\log t$. Duplicate points are shown on the curve at -49.5° C to indicate the reproducibility of the data.

Master curve and definition of the characteristic relaxation time K .—In order to construct the master curve, one may select an arbitrary reference temperature and slide the plots of $E_{r,T}(t)$ at other temperatures along the log time scale until they superpose with the relaxation curve at the reference temperature T_0 . The time scale of the master curve obtained in this way will be the time scale of the reference temperature T_0 . The relation between the relaxation modulus $E_{r,T}(t)$ at temperature T and the relaxation modulus $E_{r,T_0}(t)$ at temperature

T_0 will then be:

$$E_{r,T}(kt) = E_{r,T_0}(t) \quad (1a)$$

In Equation (1a) κ is a function of temperature alone which is completely determined if T_0 is given². At first it is necessary to choose the reference temperature T_0 arbitrarily in order to construct the master curve. Once this is done, however, it is desirable to find a less arbitrary definition of T_0 and κ particularly when different polymers are being compared.

This can be achieved as follows: the master curve of $\log E_{r,T}(t)$ vs. $\log t$ in the transition region generally passes through an inflection point. We can define a new quantity, K , at any temperature as the time (in hours) required to attain this inflection point, so that $t/K = 1$ at the inflection point at all temperatures. K has the dimensions of time whereas κ was a dimensionless quantity². The values of K and κ differ by the same numerical factor at all temperatures. Table I gives the value of K in hours for GR-S at the temperatures used to obtain the relaxation curves shown in Figure 1. The quantity K may be regarded as a *characteristic relaxation time* at each temperature.

TABLE I
TEMPERATURE DEPENDENCE OF CHARACTERISTIC RELAXATION TIME K
IN HOURS FOR GR-S AND POLYMETHYL METHACRYLATE

GR-S		Polymethyl methacrylate	
Temp. (°C)	Log K	Temp. (°C)	Log K
-64.0	2.2	40	6.60
-61.0	1.40	60	4.50
-58.8	0.70	80	3.60
-57.6	.20	92	3.15
-55.0	-0.82	100	2.20
-52.5	-1.66	110	0.00
-49.5	-2.78	112	-1.85
-47.5	-3.32	115	-3.10
-44.0	-4.7	120	-4.30
-40.0	-5.5	125	-5.70
-32.8	-6.1		

The universal master relaxation curve $Q(t/K)$ defined in Equation (1) may now be introduced. The plot of $\log Q(t/K)$ vs. $\log (t/K)$ for GR-S gum stock where K is defined as above is shown in Figure 2. The points shown on this graph are taken from the original data at the eleven different temperatures shown in Figure 1. The experimental times were divided by the K values given in Table I and then were plotted in Figure 2.

Figure 2 also shows a plot of $-d \log Q(t/K)/d \log (t/K)$ vs. $\log (t/K)$. The maximum value of this plot obviously corresponds to the inflection point of the universal master curve.

Definition of the distinctive temperature.—The temperature dependence of K for other polymers has previously been expressed by the Arrhenius relation $K = A \exp(H_{act}/RT)^4$. The apparent activation energy is obtained from the relation:

$$H_{act} = 2.303R \frac{d \log K}{d(1/T)} \quad (2)$$

For polyisobutylene the value of H_{act} was found to be approximately constant at high temperatures, increasing markedly however as the temperature is

lowered toward the glass transition (second-order transition) temperature⁴. For polymethyl methacrylate the apparent activation energy was found to go through a definite maximum⁵. This was also found to be the case with GR-S.

Figure 3 shows a plot of $\log K$ vs. $1/T$ and also a plot of H_{act} (defined by Equation 2) against $1/T$. The H_{act} vs. $1/T$ curve goes through a definite

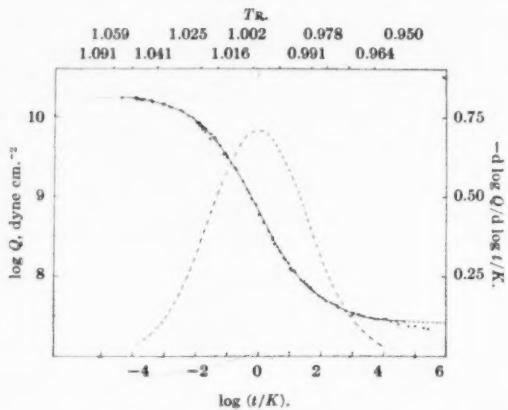


FIG. 2.— $\log Q(t/K)$ vs. $\log (t/K)$ for GR-S; also $-d \log Q(t/K)/d \log (t/K)$ for GR-S.

maximum at a certain temperature. (The plot of H_{act} vs. T goes through a maximum at the same temperature.) This unambiguously defined temperature may be regarded as a distinctive temperature for each polymer and will be denoted by T_d . For the GR-S gum vulcanize, the distinctive temperature

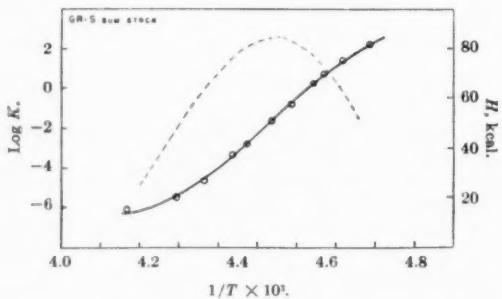


FIG. 3.— $\log K$ vs. $1/T$ for GR-S; also H vs. $1/T$ for GR-S.

T_d is approximately -53° C. This may be compared with the reported value of -61° for GR-S polymer for the second-order transition temperature obtained from the apparent discontinuity in heat capacity⁶.

Analytical expression for $Q(t/K)$ for GR-S.—Seeking an empirical expression to fit the experimental results for $Q(t/K)$, we noticed that the negative deriva-

tive of the master curve approximated a Gauss error curve, *i.e.*:

$$-\frac{d \log Q(t/K)}{d \log (t/K)} = A \exp \{ -[h \log (t/K)]^2 \} \quad (3)$$

where A and h are the adjustable parameters of the Gauss error curve. Upon integrating (3) one obtains:

$$A \int_{-\infty}^{\infty} \exp \{ -[h \log (t/K)]^2 \} d \log (t/K) = \log E_1 - \log E_2 \quad (4)$$

where E_1 and E_2 are the limiting values of the modulus at both ends of the transition region; *i.e.*, E_1 is the "glassy" modulus ($10^{10.24}$ dynes/cm.² for GR-S) and E_2 is the "rubbery" modulus ($10^{7.44}$ dynes/cm.² for the GR-S gum vulcanizate). By evaluating the definite integral in equation (4) one obtains:

$$A = \frac{h}{\pi^{\frac{1}{2}}} (\log E_1 - \log E_2) \quad (5)$$

The equation of the master curve therefore is:

$$\log Q(t/K) = \log E_2 + \frac{\log E_1 - \log E_2}{\pi^{\frac{1}{2}}} \int_{h \log t/K}^{\infty} e^{-x^2} dx \quad (6)$$

Equation (6) can be readily transformed into the more easily handled Equation (7):

$$\log Q(t/K) = \frac{\log E_1 + \log E_2}{2} - \frac{\log E_1 - \log E_2}{2} \left[\frac{2}{\pi^{\frac{1}{2}}} \int_0^{h \log t/K} e^{-x^2} dx \right] \quad (7)$$

The quantity within the brackets is the tabulated probability integral.

The quantities h and $\log E_1 - \log E_2$ were evaluated from the slope and intercept of a plot of:

$$\log \left[-\frac{d \log Q(t/K)}{d \log (t/K)} \right] \text{ vs. } \log (t/K)^2$$

(This graph is not shown in the paper.) For the GR-S gum vulcanizate, $h = 0.45$ and $\log E_1 - \log E_2 = 2.80$. The excellent fit of Equation (7) to the experimental points of the master curve is shown by the full curve of Figure 2. This curve was obtained from Equation (7) by taking $h = 0.45$, $\log E_1 = 10.24$ and $\log E_2 = 7.44$. The agreement, as can be seen from Figure 2 is excellent for temperatures ranging from -64 to -40° C. Some deviation occurs at higher temperatures.

It is clear from Equation (7) that when $t/K = 1$, $\log Q(t/K) = (\log E_1 + \log E_2)/2$. This, of course, means that $\log Q(t/K) = (\log E_1 + \log E_2)/2$ at the inflection point of the master curve if Equation (6) is valid. However, this may also be used as an alternate way to define the characteristic relaxation time K , particularly in polymers where the inflection point on the master curve is not sharply defined. In other words, K may be defined at any temperature as the time in hours required for $\log E_{r,T}(t)$ to attain the value $(\log E_1 + \log E_2)/2$.

Analytical expression for $Q(t/K)$ for polymethyl methacrylate.—The method used for GR-S is also applicable to the previously obtained¹⁵ master curve for

polymethyl methacrylate. As shown in Figure 4, the equation:

$$\log Q(t/K) = 8.85 - 1.5 \left[\frac{2}{\pi^{\frac{1}{2}}} \int_0^{0.31 \log t/K} e^{-x^2} dx \right] \quad (8)$$

expresses the experimental results for polymethyl methacrylate quite accurately in the temperature range between 60 and 125° C.

The κ values for polymethyl methacrylate used in Reference 2 were calculated from Equation (1a), using as the reference temperature $T_0 = 110^\circ$. Fortunately this definition of κ leads to a scale factor of unity for converting κ values to K values; this is because $E_{r,283}(t)$ is exactly at the inflection point of the relaxation curve after 1 hour. Thus the table of κ for polymethyl methacrylate given in Reference 2 need only have the heading changed to conform to the definition of K in this paper. The distinctive temperature T_d for polymethyl methacrylate was reported⁷ as 111° C.

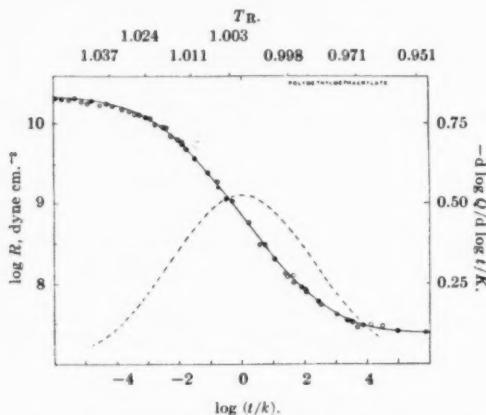


FIG. 4.— $\log Q(t/K)$ vs. $\log(t/K)$ for polymethyl methacrylate; also $-\frac{d}{dt} \log Q(t/K)/\log(t/K)$ for polymethyl methacrylate.

Variation of the characteristic relaxation time K with temperature.—If a reduced equation for elastoviscous behavior of polymers were found to be valid, one might expect that the distinctive temperatures T_d of various polymers would be corresponding temperatures. It would, therefore, be very interesting to compare the values of the mean relaxation times K_d of various polymers at their respective distinctive temperatures.

In the case of GR-S, ($T_d = -53^\circ$), $\log K_d$ is about -1.5 . In the case of polymethyl methacrylate, ($T_d = 111^\circ$), $\log K_d = -1.5$ within the limit of accuracy of our measurements. This coincidence is obviously interesting and values of K_d for other polymers should soon decide whether it is accidental.

In order to compare the temperature dependence of the mean relaxation time K for both polymers, it seemed advisable to introduce a reduced temperature, $T_R = T/T_d$, and a reduced characteristic relaxation time $K_R = K/K_d$. A complete description of each polymer can then be provided by presenting the master curve, and along with the master curve a graphical presentation of the variation of $\log K_R$ with T_R . This latter was achieved in Figures 2 and 4

by considering the abscissa of the master curves as a $\log K_R$ scale and indicating along the upper border of the graph the values of reduced temperature T_R that correspond to the experimentally observed values of $\log K_R$.

The T_R keys shown in Figures 2 and 4 for GR-S and polymethyl methacrylate are not identical. This is perhaps to be expected since the master curves themselves are not identical.

Reduced equation for viscoelastic behavior of GR-S and polymethyl methacrylate.—The master curves for stress relaxation of GR-S and polymethyl methacrylate could be made practically identical if one were to plot:

$$[\log Q(t/K) - \log (E_1 E_2)^{\frac{1}{2}}] / [\log (E_1 E_2)^{\frac{1}{2}}]$$

as a function of $h \log t/K$ as can be seen by inspection of Equation (7).

It is reasonable to speculate about the result of placing the T_R keys for the two polymers on such a reduced master curve. Since the abscissa of the reduced master curve is $h \log (t/K)$, the T_R keys can be compared by plotting $h \log K_R$ vs. T_R . As can be seen from Figure 5, such a plot gives the same curve

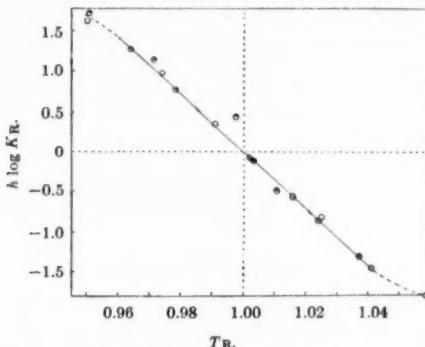


FIG. 5.— $h \log K_R$ vs. T_R for GR-S and polymethyl methacrylate:
 ○, GR-S; ●, polymethyl methacrylate.

for both polymers. This means that the same T_R key applies to both polymers on the reduced master curve. A reduced equation which applies for both can, therefore, be written:

$$\frac{\log Q(t/K) - \frac{1}{2} \log E_1 E_2}{\frac{1}{2} \log (E_1 E_2)} = - \frac{2}{\pi^{\frac{1}{2}}} \int^{\log y} \exp(-x^2) dx \quad (9)$$

where $y = (t/K)^h = (t_R/K_R)^h$ and $t_R = t/K_d$.

In the region $0.95 < T_R < 1.05$, K_R may be approximated by:

$$h \log K_R = -36(T_R - 1) \quad (10)$$

Additional experimental data on other amorphous polymers will be necessary to test the generality of equations (9) and (10).

SUMMARY

Experimental data on the stress-relaxation modulus $E_{r,T}(t)$ of a GR-S gum vulcanize at a series of temperatures in the transition region are presented,

and a "master curve" of $\log Q(t/K)$ vs. $\log (t/K)$ is thereby constructed. The characteristic relaxation time, K , for each temperature is defined and tabulated. A distinctive temperature, T_d , is observed at which the activation energy for K is a maximum. Analytical expressions are given which describe the GR-S master-curve with great accuracy. The same analytical procedure can be successfully applied to data previously obtained for polymethyl methacrylate. A reduced equation is proposed which describes the time and temperature dependence of $Q(t/K)$ in the transition region for both polymers.

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THE DIAMAGNETIC ANISOTROPY OF NATURAL AND SYNTHETIC RUBBERS *

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INTRODUCTION

The magnetic anisotropy of rubbers has previously been studied by Mme. Cotton-Feytis¹. She first observed that vulcanized commercial rubber showed some anisotropy and studied the effects of compression, stretching, and hot and cold working on crude rubber. By Krishnan's oscillation method² she measured the anisotropy of stretched rubbers, using rubber bands stretched around a glass or plexiglas disc. The anisotropy was found to increase in the early stages of elongation, but at 400 to 500 per cent elongation the anisotropy tended toward a limit, the curve of anisotropy as a function of tension having the same general shape as the curve showing variation in intensity of spots in the *x*-ray diffraction pattern of rubber with tension³.

In this work, the changes in diamagnetic anisotropy on stretching have been measured for natural rubber and for several saturated and unsaturated synthetic rubbers in an attempt to relate the changes in anisotropy with stretching to the degree of orientation of the rubbers.

EXPERIMENTAL PART

Preparation of samples.—The following rubber samples, and their descriptions, were supplied by the B. F. Goodrich Company, in the form of thin sheets approximately a millimeter thick, between two layers of cellophane⁴.

Natural rubber, No. 1 thin pale latex crepe, essentially a polyisoprene. Polybutadiene X-453, a 50 per cent conversion polymer stabilized with phenyl- β -naphthylamine, short-stopped with di-*t*-butylhydroquinone. Polybutadiene-V, a 93 per cent conversion polymer made at 50° and stabilized with 1.5 per cent phenyl- β -naphthylamine, short-stopped with hydroquinone. Polybutadiene-VI, a 73 per cent conversion polymer made at 50° and stabilized with 1.5 per cent phenyl- β -naphthylamine, short-stopped with hydroquinone. Butyl rubber (GRI-50) a polyisobutylene containing about 2 per cent of butadiene or isoprene. Vistanex, polyisobutylene of molecular weight about 100,000. Vistanex B-100, a polyisobutylene of molecular weight about 100,000. Vistanex B-120, a polyisobutylene of molecular weight about 120,000.

The rubbers were used as small rubber bands, which could be fitted around a thin rectangular slab of an isotropic or nearly isotropic substance. This slab could then be attached to a suspension for the anisotropy measurement. By varying the size of these supporting slabs, the elongation of the rubber band could be changed. Polyethylene was chosen as the material for these cores, because it has a small anisotropy, is light, and because it is rigid enough that

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thin slabs will not buckle when holding a highly elongated rubber band. A series of small rectangular slabs of polyethylene were cut from a thin sheet of polyethylene⁵. The magnetic anisotropy of each slab was measured, and the dimensions of each were found with a micrometer caliper. Each slab was weighed also.

A small portion of each sheet of rubber was dissolved in benzene to make a cement for forming rubber bands. The rubber Polybutadiene-V would not dissolve in benzene or other solvents and no rubber bands were made from this sheet.

A strip of rubber about one inch long and a half-inch wide was cut with scissors from the original sheet, avoiding any bubbles or other visible imperfections. The strip was laid on a six-inch square glass plate and the cellophane layers on both sides were peeled off with an embroidery needle, care being taken not to stretch the rubber nor to mar the surface. By use of a sharp razor blade the strip was trimmed to the desired width, 3 to 5 mm. Then the smallest polyethylene core to be used was laid across the sample with the upper and lower ends protruding about 1 mm. over the side of the strip. The ends of the strip were trimmed with a razor until they just met about the polyethylene slab. The appropriate rubber solution was applied along the two edges to be joined. These edges were then brought together, and if necessary held together until they stuck. Then a thin coat of rubber solution was applied over the join, followed by one or two more coats at half-hour intervals. When the join had dried thoroughly, the band was removed from the polyethylene core with a small needle. One or two coats of rubber solution were then applied to the inner side of the join. When the rubber band had dried completely, it was ready for use, and it was assumed that, on the polyethylene slab used in making the band, the rubber was unstretched.

Magnetic anisotropy measurements.—These were made by the Krishnan flip-angle method⁶. The equipment used and the application of the method to polymers have previously been described⁷. All magnetic measurements were made at room temperature.

The diamagnetic anisotropy of each rubber band was determined first on the polyethylene core used in making it, and then while stretched on successively larger cores. The size of the cores was limited by the necessity of having the sample hang freely in the glass tube protecting it. A number of the samples were very thin or started to tear before the largest core was reached, and the final measurements on each band were therefore less reliable than those made at lower elongations. It should be noted that the anisotropy measured was the difference between the susceptibility parallel to the direction of stretching and the susceptibility perpendicular to the direction of stretching of the rubber band.

Measurements were also made of the change in anisotropy with time, at one elongation, for natural rubber. The anisotropy was measured at one elongation after various time intervals, until the anisotropy reached a constant value. These measurements were then repeated at each of the higher elongations.

RESULTS

Table I shows magnetic anisotropy data for a typical sample of natural rubber⁸. The angle between the plane of the suspended sample and the direction of the field is given at each elongation. An angle of 0° indicates that the direction of stretching was parallel to the direction of the magnetic field when

TABLE I
MAGNETIC ANISOTROPY OF NATURAL RUBBER AT VARIOUS ELONGATIONS

Angle	Weight (mg.)	$\Delta X/g.$ $\times 10^3$ (observed)	$\Delta X/g.$ $\times 10^3$ (corrected)	$(\Delta X - \Delta X_i)/g.$ $\times 10^3$ (corrected)	Elonga- tion (%)
0°	15.00	59	97	0	0
0		88	139	43	20
0		109	155	58	57
0		142	186	89	96
0		193	247	151	151
0		268	417	320	259

the sample was in its initial equilibrium position. The weight of the rubber band is also given.

The observed value of the anisotropy, ΔX per gram, is given at each elongation of the sample. The observed values were corrected for the anisotropy of the supporting polyethylene slabs, and for effects at the ends of the polyethylene slabs. These corrected values of the anisotropy per gram are given in the fourth column of the Table. The change in anisotropy at each elongation is listed as $(\Delta X - \Delta X_i)$ per gram, where ΔX_i is the initial anisotropy of the unstretched sample. The percentage elongation of the sample is given also, taking the elongation of the unstretched sample as 0%.

In Figure 1 the change in anisotropy $(\Delta X - \Delta X_i)$ per gram is plotted *vs.* percentage elongation for all samples of natural rubber and of Butyl rubber. For each sample of each rubber, the straight line of best fit was determined by the least-squares method, and the intercepts and slopes found for all samples of each rubber were averaged to give a representative equation for each rubber.

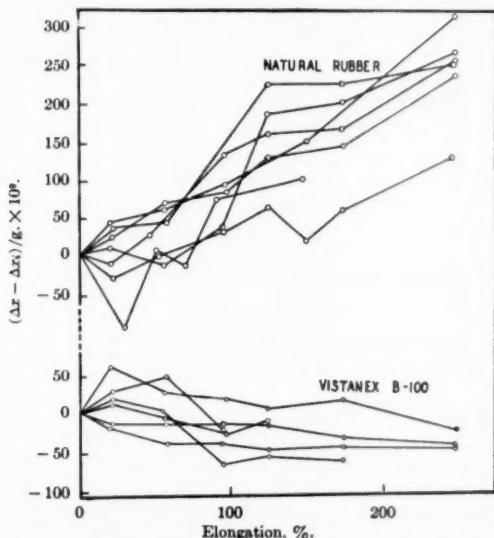


Fig. 1.—Corrected magnetic anisotropy of all samples of natural rubber and of Vistanex B-100 *vs.* percentage elongation, showing the variations in anisotropy from one sample to another of the same material.

In Figure 2 $(\Delta X - \Delta X_0)$ per gram is plotted for each rubber, using these averaged equations. Polyethylene, for which the change in anisotropy with elongation has previously been measured⁹, is included in this graph for comparison. In these graphs the curves for those rubbers which showed a larger susceptibility perpendicular to the direction of stretching have a positive slope, while the curves for the rubbers having a larger susceptibility parallel to the direction of stretching have a negative slope. The change of anisotropy with time was measured for two samples of natural rubber, and was found to be small.

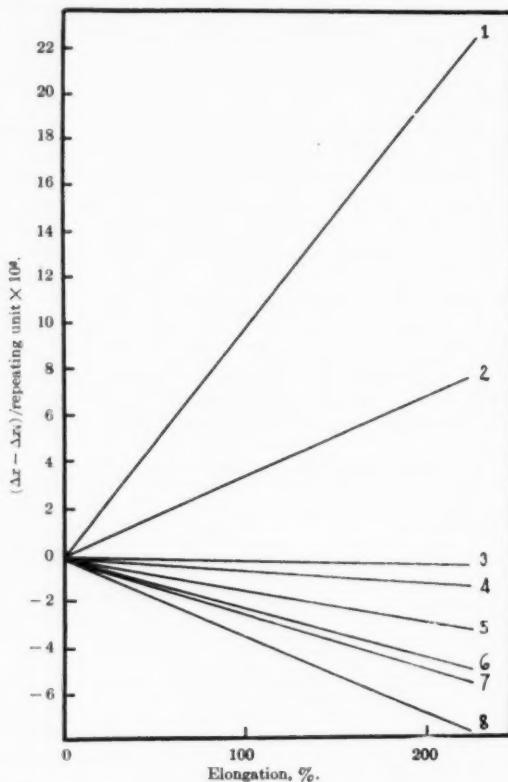


FIG. 2.—Change in magnetic anisotropy of rubber *vs.* percentage elongation (determined by method of least squares): 1, natural rubber; 2, polybutadiene X-453; 3, polyethylene; 4, polybutadiene-XI; 5, Vistanex B-100; 6, Vistanex; 7, Butyl rubber; 8, Vistanex B-120.

A source of error was introduced into the measurements by uneven stretching of the rubber bands on the polyethylene cores, and by small rips in the samples, which occurred frequently at high elongations. Thus the actual elongation of a sample was not necessarily that which would be calculated from the size of the core used. The least squares method of finding the line of best fit adjusts only the anisotropy values, and not the elongations. However, the results obtained are an indication of the relative magnitudes of the anisotropy changes occurring with elongation for each of the rubbers.

DISCUSSION OF RESULTS

The rubbers can be considered as uniaxial crystals, with the unique axis parallel to the direction of stretching. Bunn¹⁰ reports that x-ray diffraction photographs of polyethylene indicate that the electron clouds of the $-\text{CH}_2$ groups are not spherical, but are elongated in the plane of the carbon-hydrogen bonds, the plane normal to the chain axis. This distortion would lead to an increase in the mean square radii of the electronic orbits of the carbon atoms perpendicular to the chain axis, and, since the diamagnetic susceptibility of a substance in any given direction is proportional to the sum of the squares of the average electronic radii in the plane perpendicular to that direction, it would give rise to a susceptibility parallel to the chain axis larger than that perpendicular to it. Such an effect has been found for polyethylene⁹.

The principal susceptibilities of the rubbers depend on two factors. First, the long-chain hydrocarbon skeleton should have an anisotropy comparable to that of polyethylene with the larger susceptibility parallel to the chain axis. Second, the presence of double bonds, especially in a state of resonance, has been found to introduce a diamagnetic anisotropy opposite in sign to that of the saturated hydrocarbons¹¹, with the larger diamagnetic susceptibility perpendicular to the plane of the double bonds. In an unsaturated rubber, both of these effects operate, opposing each other.

Natural rubber and polybutadiene X-453, both unsaturated, show large increases in anisotropy with stretching, and have the larger principal susceptibility perpendicular to the direction of stretching, and thus perpendicular to the double bonds. The third unsaturated rubber, polybutadiene-VI, has its larger susceptibility parallel to the direction of stretching, but shows only a small change in anisotropy on elongation, the change being almost identical with that of polyethylene.

Natural rubber shows a greater change in anisotropy with stretching than does polybutadiene X-453. If the methyl group of the isoprene monomer is magnetically isotropic, the anisotropy of the isoprene and butadiene monomers should be the same, although the principal susceptibilities of isoprene would be larger than those of butadiene. Therefore the difference between the anisotropies of the two rubbers must be due to differences in orientation of the polymers. One possible explanation of such differences in degree of crystallinity is that natural rubber is the *cis*-form of polyisoprene¹², but that polybutadiene is a mixture of *cis*- and *trans*-forms. Thus natural rubber has a regular structure and crystallization can occur easily, but polybutadiene would have an irregular chain, and alignment of neighboring chains would be more difficult. Therefore polybutadiene would be more amorphous than natural rubber and would have a smaller anisotropy at any given elongation. However, Field, Woodford and Gehman¹³ found that synthetic polyisoprenes probably do not contain any appreciable amount of the *trans*-isomer, and it is quite possible that the same is true of polybutadiene.

A more likely explanation can be found on consideration of the work of Kolthoff, Lee and Mairs¹⁴ who analyzed a number of rubbers with perbenzoic acid to find the percentage of "external" double bonds, terminal or side-chain double bonds, as opposed to "internal" ethylenic double bonds within a chain of carbon atoms. It was found that natural rubber has 98.5 per cent of the theoretical unsaturation and no external double bonds, although synthetic emulsion polyisoprene has 99 per cent of the theoretical unsaturation, 13 per cent of this in external double bonds. Emulsion polybutadiene, a 44 per cent

conversion polymer, had 99 per cent of the theoretical unsaturation, 22 per cent of which was in external double bonds, while a 75 per cent conversion emulsion polybutadiene had 96 per cent of the theoretical unsaturation and 23 per cent external double bonds. The two polybutadienes considered here, Polybutadiene X-453 and Polybutadiene VI, are 60 and 73 per cent conversion polymers, respectively, and are thus comparable to Kolthoff's two polybutadienes. There must be far more branching in polybutadiene than in natural rubber; on the average there should be one side-chain, formed by 1,2- instead of 1,4-addition, to every three repeating units in the polybutadiene chain. This would decrease the possibility of crystallization on stretching, and the presence of unsaturated side-chains also increases the smaller principal susceptibility parallel to the chain axis, thus decreasing the anisotropy of the polymer. Probably the actual degree of crystallinity does not affect the anisotropy to any great extent, but rather the possibility of the chain molecules orienting themselves parallel to the direction of stretching is the important factor. Short side-chains do not interfere much with such alignment, but cross-linking tends to prevent it. The major difference between natural rubber and polybutadiene X-453 is probably the presence of unsaturated side-chains in the latter. These side-chains, if present in the ratio of one to every three repeating units in the chain, would be expected to reduce the anisotropy to about one-half that of an unbranched chain. This is about the observed decrease in anisotropy from natural rubber to polybutadiene X-453, as can be seen from Figure 2.

Polybutadiene VI appears to be almost amorphous. The number of side-chains appears to be about the same for both 50 and 73 per cent conversion polymers, according to Kolthoff's data. However, there is also a decrease in the per cent of theoretical unsaturation from 99 per cent in the lower conversion polymer to 96 per cent in the higher conversion one. If this decrease can be attributed solely to cross-linking, there is about one cross-linkage to every twenty chain repeating units in the higher conversion polymer and one cross-linkage for every seventy-five or eighty repeating units in the lower conversion polymer. A high number of cross-linkages in polybutadiene-VI would prevent the molecular chains from aligning themselves parallel to the direction of stretching to any great extent and thus decrease the anisotropy greatly. There is no obvious reason why the principal susceptibility parallel to the direction of stretching should be the larger one.

The four polyisobutylenes, Butyl rubber and the three Vistanex samples, all have the larger principal susceptibility parallel to the direction of stretching and thus to the extended chain. Since these rubbers are saturated the only contribution to the anisotropy should be that due to the broadening of electronic orbits perpendicular to the chain axis as in polyethylene. However, the principal susceptibility parallel to the chain increases much more with elongation in the polyisobutylenes than in polyethylene. The methyl groups must cause a much greater broadening of the electronic orbits perpendicular to the chain axis than do hydrogen atoms. This must also occur in natural rubber, though not to the same extent as in polyisobutylene, since natural rubber has only a quarter as many methyl groups. Even in polybutadiene the side-chains should slightly increase the susceptibility parallel to the direction of stretching, in addition to the effects of unsaturation of the side-groups. Thus in natural rubber and in polybutadiene X-453 the contribution of the double bonds to the principal susceptibility perpendicular to the direction of stretching must be even greater than is apparent from Figure 2.

Vistanex and Butyl rubber show an almost identical change in anisotropy with elongation. This indicates that the degree of orientation is the same in both, since the monomer units are the same. Apparently the molecular weight of the polyisobutylene also affects the anisotropy, for the change in anisotropy with elongation is greater in Vistanex B-120 than in Vistanex B-100. Thus there must be a higher degree of orientation in the higher molecular weight polymer. Polyisobutylene shows a very strong crystalline x-ray picture at high elongations¹⁵, and apparently the higher molecular weight Vistanex B-120 becomes crystalline at lower elongations than do the other polyisobutylenes. Vistanex lies between the high and low molecular weight polyisobutylenes, and probably has a molecular weight somewhere between the two, or at least a wider distribution of molecular weights. At very high elongations all three should approach the same anisotropy change between the unstretched and the highly stretched polymers, and Butyl rubber should also approach the same limit.

It should be noted that the change in anisotropy of natural rubber did not tend toward a limit at the highest elongations used, as reported by Cotton-Feytis¹. However, she did not find this effect at elongations below 400 per cent, which is greater than any employed here. Since she only reports the period of oscillation in and out of the field for the Krishnan oscillation method, and does not report the actual anisotropies of her rubber samples, it is impossible to tell whether or not her results at lower elongations agree with those found here.

Finally, the change in anisotropy with time, at any one elongation, was found to be small at all elongations, at least for natural rubber, and the changes were almost the same for each elongation and, therefore, would not change the slope of the curve showing the change of anisotropy with elongation.

SUMMARY

The change in anisotropy with elongation has been found for natural rubber and for several synthetic rubbers. Unsaturated rubbers have a large principal susceptibility perpendicular to the direction of stretching, because of the presence of olefinic double bonds. The differences between natural rubber and polybutadiene are attributed to the presence of unsaturated side-groups caused by 1,2-addition in polybutadiene. Probably the magnetic anisotropy of these rubbers depends, not on the actual degree of crystallinity of the rubbers, but on the ability of the long-chain molecules to align themselves parallel to the direction of stretching. Therefore the changes in anisotropy with stretching are large when there is no cross-linking, and small when cross-linking occurs to any large extent. Saturated rubbers have an anisotropy opposite in sign to that of unsaturated rubbers. This must be caused by the broadening of electronic orbits perpendicular to the direction of stretching. Apparently methyl side-groups cause such a broadening of electronic orbits in polyisobutylenes, an effect much greater than the similar effect in polyethylene.

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NUCLEAR MAGNETIC RESONANCE STUDY OF TRANSITIONS IN POLYMERS *

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INTRODUCTION

All polymers consisting of flexible long chains show a transition range on change of temperature. This "leathery" transition range separates the soft "rubbery" state from the hard "glassy" state. The transition occurs both for linear and cross-linked polymers. The location and breadth of the transition range may be changed, however, by swelling, plasticizing, vulcanizing, and loading with pigments. The transition takes place whether the polymer crystallizes or not.

This transition has all the characteristics of a certain type of transition of the second order envisaged by Ehrenfest¹. Both the specific heat and thermal expansion coefficient exhibit a finite jump in the transition range, leading to steplike curves without a lambda peak. Other physical properties also change in this range as, for example, the stress-temperature relationship which is studied in the companion paper².

Transitions of this type occur, as is well known, in inorganic and organic glasses. They also occur in simpler substances, like glycol and glycerol. These substances crystallize very slowly and, on rapid supercooling, the liquid-like molecular configurations freeze into an irregular network in contrast to the regular lattice they form on crystallization. Many nonpolymers show the lambda type of second-order transitions. Such transitions mark the onset of ferromagnetism, ferroelectricity, superconductivity, superfluidity in liquid helium, order in alloys, and order in molecular crystals. Thus it is clear that the molecular mechanisms for second-order transitions must show an unusual diversity. At present we have little exact knowledge of them.

The transitions in glasses as well as in polymers are usually accompanied by more or less pronounced time effects. It has been frequently argued that the transition itself is not an equilibrium phenomenon and does not represent a true thermodynamic singularity, but is merely a dynamic freezing in of certain rotational degrees of freedom. This important aspect of the problem will be discussed elsewhere. Here we take a view akin to that of Fowler and Guggenheim³ that all equilibria in thermodynamics are only relative or metastable, and that the applicability of thermodynamics to the experiment depends on the time scale of the experiment.

In most second-order transitions there are changes in the internal motion of groups of atoms. The nuclear magnetic absorption method⁴ or the nuclear induction method⁵ demonstrate directly such internal motions and their change on varying the temperature. This method has already been applied to the

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study of transitions in materials of relatively simple structure⁶. The present paper presents a preliminary study of transitions in polymers by nuclear magnetic absorption.

BRIEF DESCRIPTION OF NUCLEAR RESONANCE METHOD AS APPLIED TO THE STUDY OF POLYMERS AND OTHER SOLIDS⁷

In the nuclear magnetic resonance method, a substance containing nuclei of magnetic moment μ and spin I is placed in a homogeneous magnetic field H . In this field the nucleus may occupy one of $(2I + 1)$ available Zeeman levels. In the following we shall consider only the case of protons, where I is equal to $\frac{1}{2}$. Then one has only two Zeeman levels, corresponding to a parallel and an antiparallel orientation of the proton magnetic moment with respect to the applied magnetic field. The energy difference between these two levels is:

$$\Delta E = \mu H - (-\mu H) = 2\mu H \quad (1)$$

Now if an alternating field is introduced at right angles to the magnetic field H with the Larmor frequency given by:

$$\nu = \Delta E/h = 2\mu H/h \quad \text{or} \quad \omega = \gamma H \quad (2)$$

a resonant absorption will take place.

For a magnetic field H of the order of 7000 gauss and a proton magnetic moment μ equal to 1.4×10^{-23} erg/gauss, one obtains from Equation (2) a frequency ν , of the order of 30 megacycles, *i.e.*, the alternating field satisfying the resonance condition is in the radiofrequency range. The width and amplitude of the absorption line depends on the substance, *e.g.*, the polymer, containing the protons. When a substance is put into a magnetic field H , the interaction between the proton spin system and the lattice enables the spin system to attain thermal equilibrium after the lapse of time measured by a spin-lattice relaxation time T_1 . An rf field tends to disturb this thermal equilibrium of the spin system. However, the interchange of energy between the proton spins and the lattice enables the spin system to again attain thermal equilibrium provided the energy input is sufficiently small to avoid saturation. In thermal equilibrium, the fractional ratio of the population of the two Zeeman levels varies in accordance with the Boltzmann relation as $1:e^{-\Delta E/kT}$. Using the above values, this ratio is about $1/10^{-6}$. This accounts for the feebleness of the resonance absorption and the need for extremely high amplification.

A second relaxation time occurs because of the magnetic or spin-spin interaction of the nuclei, leading to an interchange of energy between the spins. The resultant spin-spin relaxation time T_2 determines principally the broadening of the absorption line width. The experimental results in this paper are chiefly concerned with this spin-spin interaction as it is modified by transitions in the substance, *e.g.*, the polymers containing the protons.

In a dielectric, paramagnetic, or ferromagnetic substance, the effective magnetic field at the site of any atom is not simply equal to the externally applied magnetic field. Superimposed on the latter there is a local field due to neighboring atoms. Similarly, the spin-spin interaction leads to the development at the site of any resonating proton of a local magnetic field H_{loc} , which in solids and glassy polymers may be of the order of several gauss. This local field causes a fluctuation of the effective magnetic field. Thus, the resonance condition is modified so that:

$$\omega = \gamma H_{\text{eff.}} = \gamma(H + H_{\text{loc}}) \quad (3)$$

implying a broadening in the resonance line width by an amount

$$\delta E = \hbar \gamma H_{\text{loc}}, \quad \text{or} \quad \delta \omega = \delta E / \hbar = \gamma H_{\text{loc}} = \gamma \Delta H \quad (4)$$

The spin-spin relaxation time can now be introduced by means of the uncertainty principle:

$$T_2 = \hbar / \delta E = 1 / \gamma H_{\text{loc}} \quad (5)$$

Since H_{loc} represents a deviation of the magnetic field from an average H , inhomogeneities of the field also broaden the line and determine, in fact, the lower limit of line width which can be observed with the particular magnet used. From the above simple picture, one would expect the line width $\delta \omega / \gamma$ due to spin-spin interaction to be of the order of H_{loc} , i.e., of the order of several gauss. In fact, most solids, including polymers in the glassy state, exhibit a line width of this order of magnitude. However, for some solids, for polymers in the rubbery state, and for liquids and gases, the line width is limited only by the inhomogeneity of the magnet used. This narrowing of the line width was first explained by Bloembergen, Purcell, and Pound⁸ as due to an averaging out of the spin-spin interaction resulting from free or partly hindered motion of the resonating protons in their surroundings. This averaging-out process is most easily understood in the extreme case of a proton residing in a freely rotating molecule, for it is clear that the rotational periods in this case are much smaller than the times associated with nuclear magnetic resonance. For water, Bloembergen, Purcell, and Pound predict a theoretical line width of 10^{-4} gauss, which in practice is, of course, swamped by the lower limit in width imposed by magnetic field inhomogeneity. For some rubbery polymers containing protons, the line width is presumably larger than 10^{-4} gauss but still less than the width due to our field inhomogeneity.

Debye⁹, in his theory of dielectric dispersion in polar liquids, introduced a relaxation time τ , defined as the time during which the reorientation of dipoles persists. In a similar way Bloembergen, Purcell, and Pound introduce a correlation time τ_c , which is related to Debye's τ by a factor of the order of unity. For the case of a polymer, $1/\tau_c$ may be taken as a measure of the average jump-rate with which the movable molecular groups change (around a single C—C bond) from one minimal position to another in, say, a threefold potential. This process, which might be termed a quasi-free rotation, will be described in more detail later. It is well known that for polar polymers, Debye's single relaxation time τ has to be replaced by several or by a whole spectrum of relaxation times. Similarly, the single correlation time τ_c introduced by Bloembergen, Purcell and Pound will have to be replaced by a whole spectrum of correlation times in the case of polymers. In the absence of a more elaborate theory a single correlation time τ_c could be used representing an average value for the spectral distribution. The effect of τ_c on T_2 and consequently on the line width has been discussed quantitatively by Bloembergen, Purcell, and Pound assuming nearest neighbor interaction between the resonating protons. The relationship between T_2 and τ_c is given by:

$$(1/T_2)^2 = C \tan^{-1}(2\tau_c/T_2) \quad (6)$$

where the constant C depends on the internuclear distance and other constants which are independent of frequency and temperature. A distinction must now be made for two cases: (a) If τ_c is much greater than T_2 , then $T_2 = (2/\pi C)^{1/2}$, which can be shown to be equal to T_2'' , the relaxation time associated with a rigid lattice. In this case, $\Delta H = 1/\gamma T_2''$, and T_2'' represents the average life-

time of the nucleus in a particular energy state or orientation. Since τ_c is much greater than T_2'' , the slow fluctuation of the internuclear fields has a negligible influence on the spin-spin interaction. (b) If, on the other hand, τ_c is much smaller than T_2 , then $T_2 = \frac{1}{2}C\tau_c$ and $\Delta H = (1/\gamma 2C)\tau_c$. In this case, the spin-spin interaction is greatly diminished and the relaxation time is increased correspondingly because of the averaging out of the local field during the lifetime of a nuclear state. Equation (6) may be rewritten in terms of a correlation frequency¹⁰ as:

$$(\delta\nu)^2 = A^2(2/\pi) \tan^{-1}\{\alpha(\delta\nu/\nu_c)\} \quad (7)$$

where $\nu_c = (2\pi\tau_c)^{-1}$ is defined as an average frequency of spatial rearrangement of a molecular complex. $\delta\nu$ is the line width on a frequency scale obtained from the observed width of the magnetic resonance line, the width of the line being taken as the distance on a magnetic field scale between the maximum slopes of the absorption signal.

The constant A in the above relationship clearly represents the line width for a rigid lattice where ν_c approaches zero. With increasing lattice motion, the line width decreases. Line widths for solids are usually of the order of a

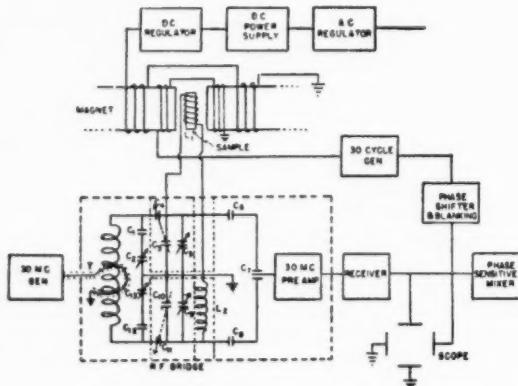


FIG. 1.—A schematic diagram of the apparatus.

few gauss, which correspond to values on the frequency scale of several tens of kilocycles. It follows then from the above relation, that absorption lines are narrowed by comparatively low frequencies, provided these frequencies exceed that represented by the half-width of the resonance line.

APPARATUS

The technique employed in obtaining and measuring the absorption signal was basically that described by Bloembergen, Purcell, and Pound⁸. A block diagram of the apparatus is shown in Figure 1. The sample (about one cubic centimeter in volume) was housed in the rf coil L_1 which is part of the tuned circuit of the twin T bridge. A General Radio 805C Standard Signal Generator supplied the 30 mc rf field. The bridge was usually balanced to 60 or 70 db, although for strong signals a lesser balance was sufficient. The unbalanced signal at resonance was detected by a Hallicrafter SX-42 receiver. For weak

signals, the magnetic field was varied over a small portion of the absorption line and the final amplification was obtained by means of a lock-in narrow band amplifier¹¹.

The magnet used to produce the static field H was a high voltage, low current electromagnet. An electronic regulator was used to hold the current stable to one part in 10^5 . A current of 300 ma was sufficient to produce the necessary 7050 gauss for observing the proton resonance. By careful lapping of the pole faces, a region near the center of the faces was located with an inhomogeneity of less than 0.1 gauss over the area of the sample used. The inhomogeneity of 0.08 gauss represents the line width obtained for a water sample whose theoretical value is of the order of 10^{-4} gauss. Line widths could be measured to an accuracy of <0.01 gauss for narrow lines and to <0.1 gauss for very broad lines. The static field was modulated by a 30-cycle field of several gauss to produce a repetitive absorption signal.

Low temperatures were controlled and maintained by a dry ice alcohol reservoir in contact with the shield housing the radiofrequency coil and sample. Above room temperature, the reservoir was filled with a suitable liquid, the temperature being controlled by an immersion-type heater.

SURVEY OF LINE WIDTHS AS AFFECTED BY VARIOUS FACTORS

LINE WIDTHS AT ROOM TEMPERATURE

Line widths at room temperature have been obtained for a number of polymers, some of which are presented in Table I.

TABLE I

	Uncured	Cured	30 parts carbon	50 parts carbon
Natural rubber	<0.08	0.16	0.18	0.67
GR-S	<0.08	0.27	0.57	0.67
Hycar OS-10	0.38		0.57	
Butyl	0.38	0.42		
S-polymer uncured	30% styrene		50% styrene	75% styrene
Line width	1.5		1.9	5.8

The natural rubber and GR-S widths shown are lower than those reported in our preliminary results¹² because of an improvement made in the homogeneity of our magnetic field. Room temperature line widths for other polymers studied may be obtained from the line width transition curves. The width of 0.08 gauss represents the minimum value that could be measured, and is attributed to magnetic field inhomogeneity. Therefore, both the unvulcanized natural rubber and GR-S may have line widths narrower than 0.08 gauss. GR-S and Hycar OS-10 are approximately 70/30 and 50/50 butadiene-styrene copolymers, respectively. The S-polymers are isobutylene-styrene co-polymers, the numbers referring to the approximate styrene content. Plexiglas is polymethyl-methacrylate.

The extremely narrow line obtained for natural rubber and GR-S makes plausible the assumption of quasi-free rotation of proton groups which is made in the statistical network theory of rubber elasticity, since the averaging out of the magnetic interaction between protons requires a high degree of mobility. The term quasi-free rotation is not to be understood as a free rotation of groups around single C—C bonds as originally envisaged in organic chemistry.

Rather, it implies that molecules or groups of molecules jump quite abruptly about the single C—C bonds in a random manner from one minimal position to another within, say, a three-fold potential. These jumps occur very rarely on a molecular time scale, and are separated by billions of oscillations about these

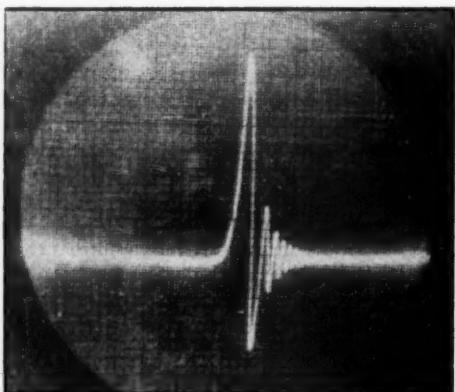


FIG. 2.—Resonance absorption line for water.

minimal positions. It is, of course, the rate ν (occurring in Equation (7)) of these sudden jumps which determines the line width and which, conversely, is inferred from the line width data. This jump rate may be of the order of 10^6 sec $^{-1}$, while the torsional oscillation frequency may be of the order of 10^{12} sec $^{-1}$.

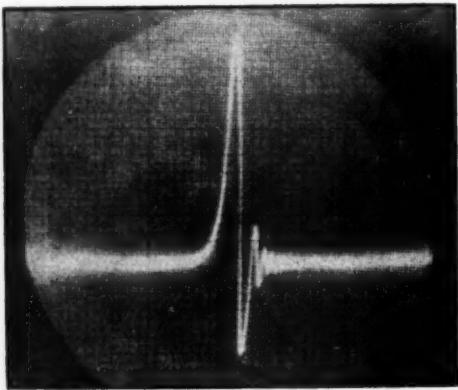


FIG. 3.—Resonance absorption line for natural rubber.

Figure 2 shows the resonance absorption line for a water sample, as viewed on an oscilloscope. It represents a plot of the rf absorption as a function of magnetic field intensity. The width of the line, as measured between points of maximum slope on the curve, was 0.08 gauss. The theoretical line width for

water is of the order of 10^{-4} gauss⁸. The absorption line for the natural rubber is shown in Figure 3. The measured value was the same as that obtained for the water sample, representing the limit of our resolution. The line width for the rubber sample is probably larger than that for the water sample, but a further comparison would have to be made by an estimate from thermal relaxation data. The occurrence of "wiggles" in both signals is a transient phenomenon characteristic of very narrow lines obtained in homogeneous magnetic fields¹³. Figure 4 shows the line shape for Butyl rubber. The line width here is several times that for natural rubber and represents the actual width, since it is above the limit of resolution of our magnetic field. Butyl rubber is a copolymer of isobutylene containing isoprene to the extent of a few per cent. The bulkier structure compared to Hevea and GR-S accounts for the greater hindrance to the quasi-free rotation in Butyl rubber, which results in a considerable broadening of the observed absorption line.

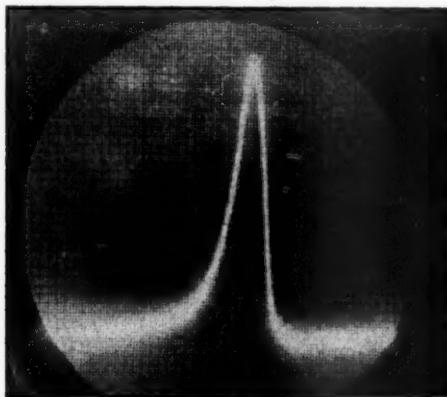


FIG. 4.—Resonance absorption line for Butyl rubber.

EFFECT OF CRYSTALLIZATION ON LINE WIDTHS

A preliminary study of line width variation with temperature in natural rubber was reported by Alpert¹⁴, and by Mrowca, Holroyd, and Guth¹².

On lowering the temperature, the signal was found to decrease in amplitude, indicating a decreased number of groups contributing to the resonance phenomena. At dry-ice temperatures, the signal was so weak as to preclude any accurate measurements, although the absorption line appeared to be quite narrow. The second-order transition in natural rubber is known to occur at about -73°C . Hence, no appreciable increase due to this cause was expected at temperatures above -73°C . Natural rubber, however, is also known to crystallize at various rates in the temperature range from 0°C to -40°C , the maximum rate occurring at about -20°C . Below -40°C crystallization is negligible.

An uncured sample of natural rubber was cooled very rapidly to dry-ice temperature and inserted into the system, which had been precooled to about -35°C . A strong signal was obtained and the line width was found to be limited by magnetic field inhomogeneity. The broadening and disappearance

of the absorption line on slow cooling could be explained, therefore, by crystallization, a process which suppresses the quasi-free rotation of molecular groups in a major fraction of the material. This was further confirmed by observing the broadening and disappearance of the line with time when the temperature was held constant at -25°C .

EFFECT OF CROSS-LINKING, LOADING AND COPOLYMERIZATION

One would expect that vulcanization and loading with carbon black would hinder internal molecular motion, and thus broaden the line as observed. One would also expect increasing amounts of styrene to have an effect similar to vulcanization or carbon black loading. The observed line widths are seen to increase as we go from GR-S to Hycar OS-10, and from S-polymer 30 to 50 and finally 75 per cent. It will be of interest to study all these effects in greater detail, in particular the effect of loading and the effects as determined by the chemical structure of the monomers.

STUDY OF LINE WIDTH THROUGH THE TRANSITION RANGE

Hycar OS-10, Hycar OR-15, polymethylmethacrylate, and polystyrene do not crystallize. Hence, line widths can be studied in these materials as a function of temperature without the complication introduced by crystallization.

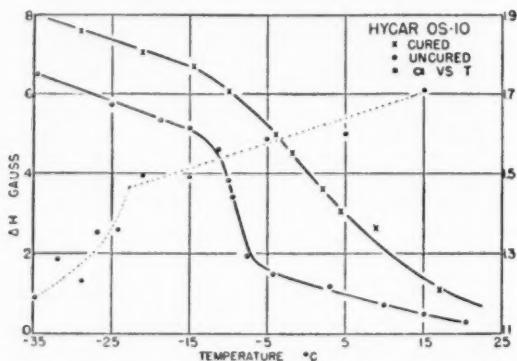


FIG. 5.—Solid curves show line width vs. temperature for cured and uncured Hycar OS-10. The dotted curve shows the linear thermal expansion coefficient $\alpha \times 10^4$ vs. temperature.

Figure 5 shows the transition curves for uncured and cured Hycar OS-10. For the cured sample, the transition range is considerably broader than for the uncured stock. The line-width change is surprisingly sharp for a material so inhomogeneous and irregular. It seems plausible to consider the change as a three-step process. The initial increase in line width as the temperature is lowered could be associated with a gradual decrease in the free volume of the molecules. This interferes with the relative motion of adjacent chain segments. The sudden increase in line width as the temperature is lowered still more suggests a fairly abrupt cessation of the quasi-free rotation about single C—C bonds. The final step, a further gradual increase in line width, could be explained by assuming a further gradual hindrance to the sliding of adjacent

segments past each other. Conversely, starting with increasing temperatures, one would assume that holes must first be created for motion of the segments before quasi-free rotation in the segments can set in. As Figure 6 shows for polystyrene, the line width should finally level off on both sides of the transition curve. This leveling off seems to start at the temperature at which a discontinuity in the curve for the thermal expansion coefficient (α) vs. temperature occurs. This is shown in Figure 5. It is likely that this discontinuity marks the appearance of free volume, making plausible our tentative interpretations. The α vs. T curve dotted in Figure 5 was obtained by differentiation of the volume-temperature relation in Figure 13 of the companion paper² and, therefore, shows some spread. The α vs. T curve refers to the cured stock.

This three-step transition must be attributed to forces involving only near neighbors. The sudden change in line widths suggests that it is due to a cooperative effect, such as the formation of domains in which molecular motion is impeded. These domains, however, must be assumed too small to be detected by customary x-ray diagrams. One would expect that abrupt changes in the elastic properties of the material should accompany such a suppression of

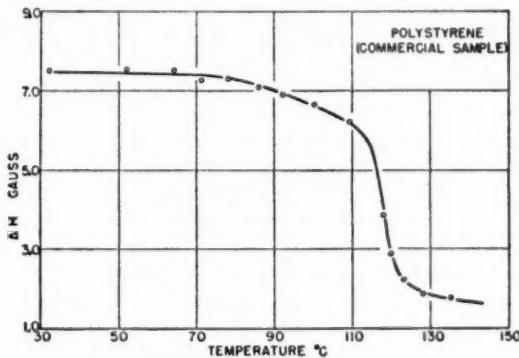


FIG. 6.—Line width vs. temperature for a commercial polystyrene sample.

internal motion. It is reasonable to assume that curing would tend to provide additional hindrance to group motion, and that it would interfere even more strongly with the formation of cooperative domains, just as it does in the case of crystallization in natural rubber. Thus, one may explain the larger initial line width and the more gradual change in ΔH observed in the cured Hycar OS-10.

In contrast to Hycar OS-10, the line width transition for Plexiglas, shown in Figure 7, is more gradual. The initial line width is considerably higher, as one would expect in view of the polar character of the material.

In Figure 8, the line width transition for Hycar OR-15 is compared with that for Hycar OS-10. The higher initial and final values and the more gradual change in ΔH obtained for Hycar OR-15 are not surprising in view of the presence of polar nitrile groups attached randomly along the chain. The α vs. T curve (lower dashed curve in Figure 7 arbitrary units) also shows a jump to the left of the inflection point in the ΔH vs. T curve, as was the case for Hycar OS-10. The α vs. T curve was obtained by differentiation of a volume temperature curve¹⁵.

Bekkedahl and Scott¹⁶ have measured the specific heat of crude Hycar OR-15 over a temperature range from 15° to 340° K. The specific heat-temperature curve (upper dashed curve in Figure 8) shows an abrupt increase in heat capacity by about 40 per cent at a temperature of 250° K. The shapes of the α vs. T and C_p vs. T curves are somewhat similar. The difference in the temperature at which the jump occurs may be explained by the fact that the

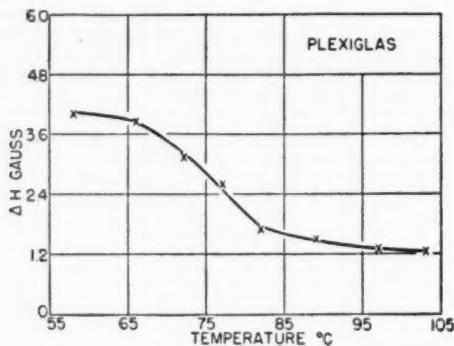


FIG. 7.—Line width vs. temperature for Plexiglas.

α vs. T curve was obtained for a loaded (30 parts E.P.C.) and vulcanized stock, while the C_p vs. T curve was obtained for the crude material. Both vulcanization and carbon black loading tend to shift the jump to a higher temperature, as illustrated in Figure 5, where a comparison is made for a crude and a vulcanized material.

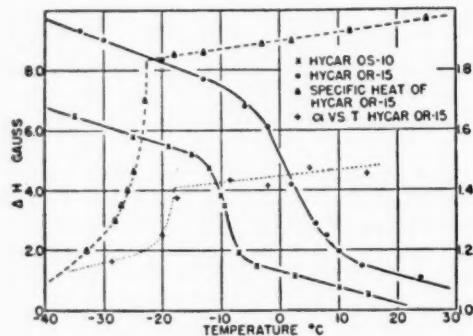
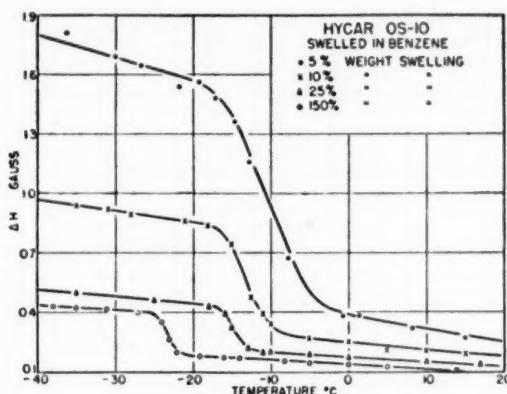


FIG. 8.—Solid curves show the line width vs. temperature for uncured Hycar OS-10 and Hycar OR-15. The upper dotted curve is the specific heat in arbitrary units vs. temperature for Hycar OR-15. The lower dotted curve shows the linear thermal expansion coefficient α in arbitrary units vs. temperature for Hycar OR-15.

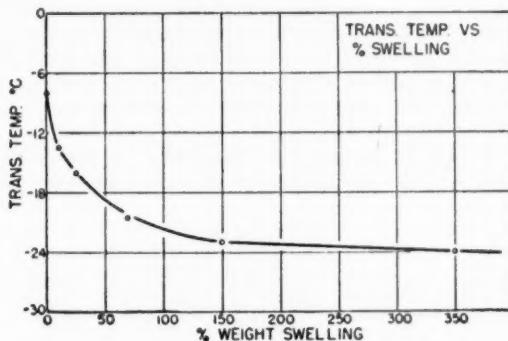
The hardening of polymers is undoubtedly due to either inter- or intramolecular interactions on a microscopic scale. Qualitatively, one would think that for polymers (such as Hevea rubber for example) which readily crystallize, the effect of intermolecular forces is dominant. On the contrary, for polymers which crystallize slowly or not at all one would think that the intramolecular

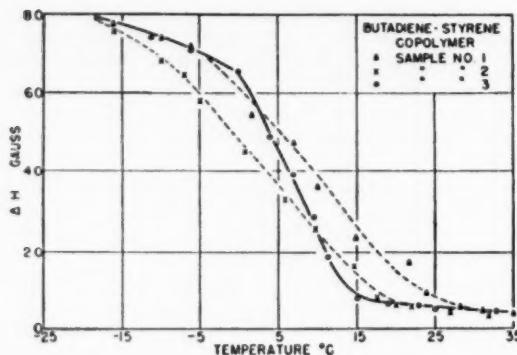
FIG. 9.—Line width *vs.* temperature for Hycar OS-10 swelled in benzene.

forces should play an important role. In the latter case, the energy barriers to quasi-free rotation may be considerably higher than in the crystallizing polymer. In the interest of gaining some insight into this mechanism, a study of line widths through the transition region was made on samples swollen in benzene.

The absorption line width for pure benzene was investigated by Andrew¹⁷ over a temperature range from a few degrees Kelvin up to the melting point. No anomalous behavior in the benzene absorption line was found between 120° K and the melting point. The line width over this region of temperatures was found to have a constant value of 3 gauss. The amplitude of the absorption signal obtained for the unswelled polymer was several orders of magnitude greater than that obtained for pure benzene. The contribution to the signal from the benzene in the polymer was, therefore, negligible. The comparatively narrow lines obtained for swollen Hycar OS-10 was attributed to the polymer.

The Hycar OS-10 samples were swelled 5, 10, 25, and 150 per cent by weight, the numbers representing parts by weight of benzene added to 100 parts of

FIG. 10.—Transition temperature *vs.* per cent swelling for Hycar OS-10.

FIG. 11.—Line width *vs.* temperature for three butadiene styrene copolymers.

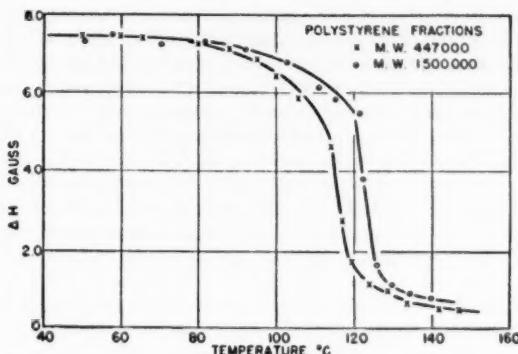
polymer. The samples were allowed to swell at room temperature over a period of several days to insure uniformity. The results are presented in Figure 9. As little as 5 per cent swelling produces a drastic change in the initial line width and the transition temperature. The initial line width of 8 gauss at a temperature of -35°C for the unswelled sample is reduced to about 1.8 gauss, and the line transition temperature is shifted to a lower value. Increased swelling gave progressively lower starting line widths and lower transition temperatures. The line widths at the higher temperatures likewise become narrower until they were finally determined solely by magnetic field inhomogeneity. Figure 10 shows the change in transition temperature as a function of swelling. The decreased line width with increased swelling throughout the entire temperature range shows that, in the unswelled glassy state, the line width is mostly due to intermolecular interaction, since swelling tends to increase the effective distance between chains and thereby decrease the interaction between adjacent chain molecules. Thus, more holes (or a larger free volume) are provided for motion of the chain segments. From the present work, however, no quantitative conclusions can be drawn as to the relative amounts of inter- and intramolecular interaction involved in the transition range. The results do indicate that intermolecular interactions seem to predominate at least for Hycar OS-10. The probability of phase separation because of freezing-out of benzene will have to be considered, however. Further swelling studies are underway.

Figure 11 shows line width transitions for three butadiene styrene copolymers which have been studied by dynamic mechanical methods at a frequency of 0.2 cycles per second¹⁸. The available data for these three samples is listed in Table II.

The line transition temperatures for Samples 1 and 2 correspond quite well with those obtained by the mechanical test method. Sample 3, however, shows

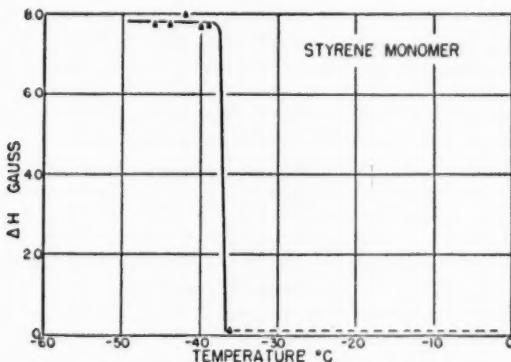
TABLE II

Sample	Styrene charged	Styrene analyzed	% gel in benzene	% swelling index in benzene	Intrinsic viscosity	Transition temp.
1	60	60	66.6	65.8	0.639	7
2	60	57.5	—	—	0.612	4
3	60	54.2	0.5 to 1	—	1.58	-5

FIG. 12.—Line width *vs.* temperature for two polystyrene fractions.

a somewhat anomalous behavior. The relatively greater sharpness of the transition would indicate greater homogeneity of material than was realized in the first two samples. The increased transition temperature is consistent with the higher intrinsic viscosity, as seen in Table II.

Line-width transitions have also been investigated for two closely cut polystyrene fractions. The molecular weights of the samples are 1,500,000 and 447,000, respectively. The dynamic mechanical properties have been found to be independent of the molecular weight over this range of fractions¹⁹. The variation of the absorption line width with temperature for these fractions is shown in Figure 12. The transitions to narrower line widths are quite abrupt when compared to a commercial polystyrene sample (see Figure 6), indicating that the broadness of the transition region may be at least partially due to a distribution in chain length which characterizes an unfractionated polymer. The transition temperature shifts with increasing molecular weights to higher values. Below the transition region, the line width for all fractions, as well as for the commercial sample, levels off to a common value of about 8 gauss. At temperatures above the transition, the line widths, in all cases, seem to fall

FIG. 13.—Line width *vs.* temperature for styrene monomer.

off to a value of the order of one gauss. A further decrease in line width to lower values was observed at higher temperatures but was not studied in detail.

The line width obtained for styrene monomer was investigated over a temperature range from room temperature to -45°C . As shown in Figure 13, the width remained constant, limited by field inhomogeneity from room temperature to -35°C . This behavior is characteristic of liquids. A very sharp rise to a value of 8 gauss for H was obtained at -35°C , a behavior usually observed at the melting point of crystalline materials. Styrene monomer is reported to have a melting point of -30.56°C . The sample used was not freshly distilled, so it may have been partially polymerized in spite of the presence of an inhibitor. The line widths for crystallized styrene and glassy polystyrene are about the same.

A ΔH vs. T curve for polyethylene was obtained by Newman²⁰. It shows a transition region about as broad as the one obtained for Plexiglas.

SURVEY AND DISCUSSION

What conclusions about the mechanism of the transition in polymers can be drawn from our work? Before we attempt to answer this question, it may be of interest to survey briefly some other work on transitions in nonpolymers by nuclear magnetism, in so far as this work is relevant to our discussion. Recent investigations have been reported by Alpert¹⁴, Gutowsky and Pake¹⁰, Andrew¹⁷, and Sachs, Turner, and Purcell²¹. A survey of the available data on the materials studied by nuclear absorption leads to the following considerations.

A decrease of the line width with increasing temperature resulting in an inflection point in the line width vs. temperature curve must necessarily be attributed to the onset, or increase in frequency, of the motion of molecular groups containing protons. This, however, does not exclude the possibility of internal motion below the inflection point, if it occurs at such a low frequency or is limited to such a small fraction of the material that it is not detectable by line absorption. The existence of an inflection point in the width vs. temperature curve, on the other hand, is not sufficient for the occurrence of a corresponding change in the macroscopic properties, such as specific heat or thermal expansion. This has been shown to be the case for some of the hydrocarbons, such as 1,1-trichloroethane, 2,2-dimethylpropane, ethyl bromide¹⁰, benzene, anthracene, and ammonium. By measuring the thermal relaxation time (T_1), Purcell, Sachs, and Turner²¹ were able to show that, for benzene and the ammonium halides, there are too few molecules participating in the line width transition to show in a corresponding change of macroscopic properties. The converse situation may also occur. A transition showing in an anomalous specific heat, for example, is not necessarily detectable by a corresponding change in the line width. The specific heat anomaly in 2,2-dimethylpropane is one such example. An interesting example if furnished by the transition in methane at 20°K . In this case, a specific heat anomaly does occur. The transition was interpreted as due to the activation of the rotational rather than the vibrational degrees of freedom. However, accurate measurements made by Thomas, Alpert, and Torrey²² did not show any change of the line width through this transition range; although a change in the relaxation time T_1 was observed. Therefore, the interpretation of this transition as being due to the onset of rotation is untenable. It should probably be attributed rather to the onset of directional order. Interestingly, T_1 was found continuous across the melting point.

From the steepness of the step in the line width vs. temperature curve, some

conclusions can be drawn, in principle, about the nature of the transition. A steep transition may be due to a cooperative phenomenon, whereas a more gradual one may correspond to a noncooperative one. The latter, of course, cannot be called a transition in a thermodynamic sense. In practice, it seems difficult to draw the line between a cooperative and a noncooperative type of transition, particularly in the absence of a theory for the transition in question. This is exemplified by the work of Gutowsky and Pake on perfluoroethane¹⁰. From the specific heat anomaly at 104° K, one would, perhaps, conclude that this second-order transition is of a cooperative nature. However, if the step in the width *vs.* temperature curve is broad, and especially if there is no corresponding change in macroscopic properties, *e.g.*, the case of 1,1,1-trichloroethane, reported by Gutowsky and Pake¹⁰, it is perhaps more reasonable to infer a noncooperative phenomenon.

If from the change of macroscopic properties one can conclude that the transition is cooperative, then it may be possible to decide between various possible mechanisms responsible for the transition. Alpert¹⁴, in particular, has tried to decide in this manner whether the transition involved a change from vibration to rotation, the mechanism assumed by Pauling²³ and Fowler²⁴, or a change from order to disorder, as postulated by Frenkel²⁵ and Landau²⁶. For a finer distinction, it would be of interest to show that, for instance, if the specific heat data can be equally well represented on the basis of either assumption, the line width change computed on the basis of Fowler's model differs greatly from that given by Frenkel and Landau's model. As pointed out by Alpert, an order-disorder transition cannot be inferred from line width *vs.* temperature data alone. Both a gradual as well as a more abrupt transition in ΔH are compatible with an order-disorder transition.

It is evident that although line width *vs.* temperature data are of great value, they must be supplemented by other measurements in order to reveal the nature of the mechanisms involved in transitions. If this is true in the case of simpler substances, it is even more so in the case of polymers. It is for this reason that a comprehensive program was undertaken at Notre Dame to measure also the following relationships through the transition range. (1) Thermal expansion coefficient (α) *vs.* temperature, (2) length *vs.* temperature (at constant force), (3) stress *vs.* temperature (at constant extension), (4) stress *vs.* relaxation (at constant extension), (4) stress *vs.* relaxation (at constant temperature), and (5) dynamic measurements (sound transmission).

We discuss here briefly only the α *vs.* T relationship, since it refers to the unstretched state, the state employed in the nuclear absorption experiments. As seen in Figures 5 and 8, both Hycar OS-10 and Hycar OR-15 show a discontinuity in the thermal expansion coefficient. It is plausible to assume a similar behavior in the C_p *vs.* T curves so that it is sufficient to consider only the α *vs.* T curves. The discontinuity in the α *vs.* T curve for both of the above polymers, as well as for polystyrene, is about 15° C below the inflection point in the ΔH *vs.* T curve. As a molecular mechanism responsible for the discontinuity in the thermal expansion coefficient, it has been tentatively assumed that it is connected with the formation of holes in the polymer which make possible a greater degree of mobility in the chain segments. The inflection point in the absorption line width on the other hand has been attributed to the onset of quasi-free rotation around a single C—C bond. Regardless of whether these assumptions are true or not, the occurrence of discontinuities (in roughly the same temperature region) in a macroscopic property and in the line width shows that a macroscopically observable number of molecular groups partici-

pate in the processes leading to a narrowing of the line width. From this alone it does not follow, of course, that the transitions in polymers are of a cooperative character, although this qualitative inference was drawn from the steepness of the jump in the line width of Hycar OS-10. It was also concluded from the effect of swelling that the line width in the glassy state is mostly due to intermolecular interaction. Furthermore, the line width in crystallized styrene seems to be about the same as in glassy polystyrene, showing that, in the glassy polymer, the protons are in the same local field as in the crystallized monomer. The specific volume is larger in the glassy than in the crystalline state. The volume-temperature relationship for polystyrene shows an anomaly in the transition region. The location of this transition region has been shown to depend on the rate of cooling. No such time effects were observed in the line width-temperature curves during the relatively short times necessary to make the measurements. The line width data were obtained by successively lowering and raising the temperature with no observable hysteresis. However further investigation will be necessary regarding such things as time effects, the effects of stress in the material, etc., and how these effects are reflected in the line width, line shape, and the thermal relaxation item. The preliminary results reported in this paper will have to be supplemented by further experimental and theoretical work, which, when properly correlated, should help to clarify the mechanism involved in polymer transitions.

SUMMARY

Nuclear magnetic resonance absorption line widths have been studied for several high polymers. The proton line widths were studied in a field of 7000 gauss and at a frequency of about 30 mc. Line widths obtained for Hevea rubber and GR-S were very narrow, indicating a large degree of "quasi-free rotation" in these materials. Vulcanization, carbon loading, copolymerization, and crystallization produced a broadening of the lines, as expected from the hindrance to internal motion introduced by these factors. Line width transitions as a function of temperature were observed for several polymers. Linear thermal expansion coefficients and specific heat *vs.* temperature curves have breaks in the region of line transitions for the polymers studied. Swelling of polymers with benzene produced a narrowing of the absorption line throughout the line transition and lowered the transition temperature. Vulcanization broadened the transition range and shifted it to higher temperatures. Of two closely cut fractions of polystyrene, the larger molecular-weight sample exhibited a line transition range at a higher temperature. The styrene monomer as well as the two fractions exhibited the same low-temperature line width of about 8 gauss. The line-width transitions were also studied for three butadiene-styrene copolymers at temperatures where anomalous behavior was found in dynamic measurements. The theoretical implications of these experimental results, together with a survey of other pertinent work, indicate the possibilities of the nuclear resonance method as applied to the study of high polymers in conjunction with other methods.

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STATISTICAL KINETICS OF HEVEA RUBBER CYCLIZATION *

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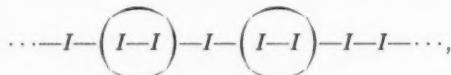
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INTRODUCTION

Standard chemical reactions can often be carried out, not only on the customary small organic molecules, but equally on regular, high-molecular-weight polymers. In such cases statistical effects may sometimes be observed to influence both the kinetics and the final composition of the products, whereby light may be shed on reaction mechanism and on structure. In simple cases two identical adjacent repeating units of a polymeric chain cooperate in an individual irreversible reaction step, usually in order to achieve a ring structure. If the unit be denoted by I , and the polymer chain by I_n or



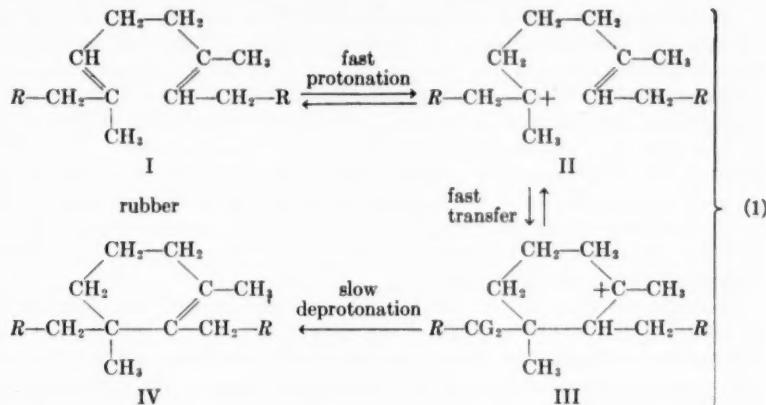
one may picture the following partly reacted section of a polymer chain:



in which the ringed couples are supposed to have reacted to form rings. Since the isolated I unit lying between the two rings shown is actually precluded from later reaction for want of a partner, the reaction cannot proceed to stoichiometric completion. Flory¹ calculated the proportion of these "widows" (isolated units) in the final polymer to be $1/e^2$ (i.e., 13.53 per cent) of the original I units, on the assumption that at each stage every couple of adjacent unreacted units has an equal chance of reaction. This result is practically independent of the degree n of polymerization, provided n exceeds about 15 or 20. Flory¹ and Wall² extended the calculation to the more complicated reactions of copolymers, and obtained results of importance for the experimental investigation of the arrangement of monomer units in the chain³. Marvel and Levesque³ and, Gordon⁴ pointed out that the cyclization of rubber is subject to this statistical effect and that analytical data on the unsaturation percentage of cyclized rubber by Fisher and McColm⁵, which were previously unintelligible, actually provide the best known experimental verification of Flory's theory. The kinetics of this cyclization, catalyzed by 70 to 80 per cent sulfuric acid, were studied⁴ by an emulsion technique on the basis of measurements in a diffusion gradient tube of the density of purified samples of the flocculated

* Reprinted from the *Proceedings of the Royal Society (London)*, Series A, Vol. 204, pages 569-585 (1951).

polymer. The mechanism supported by this work was:



Two of the original isoprenic units *I* (viz. $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2=\text{CH}-\text{CH}_2-\text{R}$) in rubber

here join to form a ring such as *IV*, and a theory was deduced for the statistical kinetic effect. This is due, of course, to the variations in status of an *I* unit as regards its chance of reacting, according to the number of its neighbors (0, 1, or 2) already reacted at time *t* during the reaction. The effect should manifest itself in a deviation from unity of the reaction order, initially to 1.5, and at the end of the reaction to about 1.16. Such deviations were not detectable by the gradient tube technique, and the present work was undertaken to confirm the rate equation by a more sensitive dilatometric method.

The chief value of the accurate confirmation actually obtained below lies in the consequent proof that the polymer forms part of the activated complex which determines the rate of the reaction. Such complexes involving polymers (*c.f.* the propagation step of polymerization) are interesting as regards the entropy of activation and in other ways. Many simple diisoprenic terpenes such as dihydromyrcene cyclize under similar conditions as rubber, and undoubtedly by an analogous mechanism. Since they are not subject to the statistical effect under discussion, however, they do not lend themselves to this direct demonstration of their participation in the rate-controlling process. In fact, kinetic measurements on these terpene cyclizations are still not available, though the emulsion technique should render them quite feasible⁶, and the polymer rubber has proved to be a suitable model compound for the lower terpenes, not only because of its advantageous statistical effect, but also for its ease of manipulation. Apart from throwing light on the role of the polymer in the mechanism, the measurements here reported strengthen the conclusions concerning the part played by the sulfuric acid. The fair correlation between reaction rate and Hammett's acidity function previously noted is quantitatively confirmed. The conclusion that deprotonation rather than protonation is rate-determining still appears to hold, though one of its supports is weakened by a reduction in the accepted frequency factor resulting from these more precise measurements.

DERIVATION OF THE STATISTICAL KINETIC EQUATION

It will be assumed that cyclization is initiated by suitable activation on an isoprene unit I in the rubber chain, followed by attack of this unit on its right-hand neighbor to form a ring (e.g., as in (1)), provided this neighbor has not already cyclized. The relative rates of these two steps, and the degree of reversibility of the first step (activation), affect only the meaning of the overall rate constant k_s of the statistical kinetic equation deduced below. Nor is the equation affected if activated units are allowed to cyclize with their left as well as their right neighbors at rates remaining proportional to each other. The law of mass action in terms of weight concentrations is assumed, and the derivation may be visualized as applied to one rubber chain with N (Avogadro's number) units, weighing 68 grams.

Imagine the chain cut at time t into chain segments and ring segments by severing all junctions between rings and uncyclized units, or between one ring and another. Denote the weight fraction of ring segments by r , this being a convenient measure of the degree of cyclization attained. The weight fraction of chain segments of exactly k adjacent I units may be denoted by i_k . Thus:

$$r + \sum_1^{\infty} i_k = 1 \quad \text{and} \quad dr/dt = - \sum_1^{\infty} di_k/dt \quad (2)$$

The exact rate equation for the growth of r is:

$$dr/dt = k_s \sum_{k=1}^{\infty} i_k (k-1)/k = k_s (1-r - \sum_{k=1}^{\infty} i_k/k) = k_s (1-r - (N_c/N)) \quad (3)$$

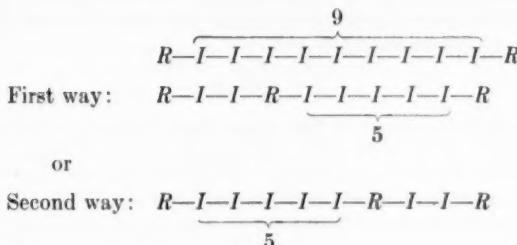
This is deduced by noting that rings are formed from the various chain segments comprising k adjacent I 's at rates proportional to i_k (law of mass action), but also proportional to $(k - 1)/k$, because each segment contains one out of its k units which is ineffective. The ineffective unit is the one at the right end, whose activation cannot lead to cyclization for want of a right-hand partner.

In the second equality of (3), the term $\sum_1^{\infty} i_k/k$ represents the deviation from first-order kinetics, and in the third equality this is equated to N_c/N , where N_c is the total number of chain segments irrespective of length.

The weight fraction i_k has a rate of change which is the balance of its rate of formation and rate of decay:

Thus its rate of chance is proportional to the number k of I units involved. The term $k + 2$ under the summation sign indicates that the chain segment with k units can be created only from segments having at least two extra units. The multiplier $2/n$ affecting i_n applies, because activation of two only out of the n units in an n -chain is favorable to such a creation. For instance, a segment of five can be created out of one of nine units in the following two

ways:



The term in (4) for the rate of decay is explained as the similar terms in (3). One can simplify the system of Equations (3) and (4) by eliminating all fractions except r , i_1 and i_2 :

$$dr/dt = k_s(1 - r - i_1 - i_2/2 - di_1/dt) \quad (5)$$

Further simplification, leading to the exact functional dependence of r alone on t , though theoretically possible, seems difficult. A very satisfactory approximate solution will now be derived by estimating the term N_e/N in (3). This solution will be integrable, will agree with the exact solution asymptotically at the beginning ($r = 0$) and end ($r_f = 0.8647 = 1 - 1/e^2 = 1 - i_f$), and will rest intermediately on a plausible physical picture of the approximate distribution of the segments.

If N_r is the total number of rings at any time t , we have:

$$N_r/N = \frac{1}{2}r \quad (6)$$

Let X be the fraction of the rings which are neighbored on the right by another ring, *i.e.*, a parameter measuring the degree of clustering together of the rings in the distribution of rings and chains during cyclization, so that

$$N_e/N = (1 - X)N_r/N = \frac{1}{2}(1 - X)r \quad (7)$$

since the number N_e of chains is equal to the number of those rings which are not neighbored by a ring on the right. The rate Equation (3) becomes

$$dr/dt = k_s(1 - r - \frac{1}{2}(1 - X)r) \quad (8)$$

At the beginning of cyclization, when r is very small, X must approach zero, while later as r grows, X will grow. Putting X equal to zero, the initial rate equation becomes asymptotically:

$$dr/dt = k_s(1 - 1.5r), \text{ initial reaction (1.5 order)} \quad (9)$$

This law does not represent the further course of the reaction, *e.g.*, it brings cyclization to an end ($dr/dt = 0$) when $r = 0.6667$ instead of 0.8647. To find X approximately as an increasing function of r , one notes that the isoprene unit lying just to the right of a ring may either be found cyclized with its right neighbor or not, and that X is the ratio of the probabilities of these two events. If we choose an isoprene unit entirely at random (without requiring it to lie to the right of a ring), the probability of its being found cyclized with its right-hand neighbor—the same as that of being found cyclized with its left neighbor—is $\frac{1}{2}r$. The probability of its not having cyclized with its right neighbor is $1 - \frac{1}{2}r$, and the ratio of the two events of interest is accordingly $r/(2 - r)$ for an

entirely arbitrarily chosen unit. Assuming that this represents also the required ratio for a unit lying just to the right of a ring, an assumption probably near to the truth, there results:

$$X = r/(2 - r) \quad (10)$$

One can test this assumption at the end of the reaction by substituting (10) in (8) and putting dr/dt equal to zero. Solving for r , one obtains $r = 1$ instead of 0.8647 as the final degree of cyclization. It is clear that the clustering tendency X of the rings at the end of the reaction has been somewhat overestimated by (10), but a mere 10 per cent adjustment in X is required, as shown by the term 0.902 in (11), to obtain the correct asymptotic behavior ($r_f = 0.8647$) in (12):

$$X = (r/(2 - r)) \times (e^2 - 3)(e^2 + 1)/e^2 - 1 = 0.902r/(2 - r) \quad (11)$$

and by substitution in (8):

$$dr/dt = k_s(1 - r - (\frac{1}{2}r)(1 - 0.902r/(2 - r))) \quad (12)$$

On the basis of the underlying physical meaning, there is little reason to suppose that X will deviate at all seriously from (11) in the earlier parts of the reaction, where in any case the Equation (12) becomes progressively less sensitive to such deviations. Further adjustments are accordingly not warranted, and the desired approximate rate equation (12) is integrated to:

$$t = F(r) - F(r_i) = k_s \{ -0.3569 \log (0.8674 - r)/(1.187 - r) - 0.5909 \log ((1.0257 - r)^2 - 0.259) - 0.4846 \} - F(r_i) \quad (13)$$

where r_i is the integration constant $F(r_i)$ denotes the initial degree r of cyclization. It is shown in (5) that experimental data confirm this equation in preference to a first-order law.

THE EQUILIBRIUM POLYMER AND ITS STRUCTURE

The statistical kinetic theory of Equations (3) and (4) and the statistical thermodynamic theory of Flory¹ can be unified and checked against each other. The following infinite series is postulated:

$$di_1/dt = - \sum_{n=1}^{\infty} (S_n/n)(di_n/dt) \quad (14)$$

and permissible values of the coefficients S_n found by comparing coefficients of i_n in Equation (4), using successively the values $k = 1, 2, 3$, etc. The result is:

$$S_n = 2(1 + S_3 + S_4 + \dots + S_{n-2})/(n - 1) \quad (15)$$

which is precisely Flory's Equation (3) for the number S_n of units I out of an n -chain which will by average be "widowed" in the whole course of the reaction. Integration of (13) yields:

$$i_1 = i_f - \sum_{n=1}^{\infty} S_n i_n/n \quad (16)$$

which correctly asserts that the current fraction i_1 of widows at time t is equal to the final value minus the fraction yet to be widowed from among all the chain segments remaining at that time. The distribution function of rings and chain segments during, or of R and I units at the end of the reaction, though implicit

in Equations (3) and (4), has not been solved. A reasonable model with a calculable distribution function for the statistically cyclized rubber can be derived. It correctly contains 13.53 per cent *I* units and 86.47 per cent *R*'s by weight, *i.e.*, about three rings to an isoprene unit, in a random co-polymer structure schematized thus



As cyclization is irreversible, two *I*'s must not come together. The model is constructed by imagining $3 \times 13.53 = 40.59$ per cent of a monomer *IR*, consisting of an isoprenic unit flanked on its right by a ring, to copolymerize randomly with 59.41 per cent of a monomer *R*. The distribution function of this model is readily calculated, and from it the interesting conclusion can be drawn that 51.54 per cent by weight of the unit *RIR* can be cut from the cyclized rubber by judicious splitting of links in the polymer chain (17). This shows the usual representation of cyclized rubber as $(R)_n$ to be quite inadequate.

EXPERIMENTAL

About 1300 grams of acid latex was compounded, essentially as described in previous reports⁷, by mixing Dunlop 60 per cent Hevea rubber latex with a stabilizer and sulfuric acid. Four kinetic runs were undertaken over a period of 4 months by following the volume change of the latex during cyclization in the thermostatically controlled Pyrex dilatometer shown schematically in Figure 1. At elevated temperature, the stem of the dilatometer passed through a lid covering the thermostat (not shown), and the control was to one-thirtieth degree or better. The fifth run, recorded in Table 1, was intended as a check, being based on a latex compounded from a different shipment, and by its excellent concordance proves that the rates are reproducible. The run numbered 4 was on a latex obtained from the acid latex of runs 1 to 3 by dilution with a known amount of water, to check the influence of acidity on rate⁸. The full details of measurement and checks quoted hereafter refer to the model run 3, comprising

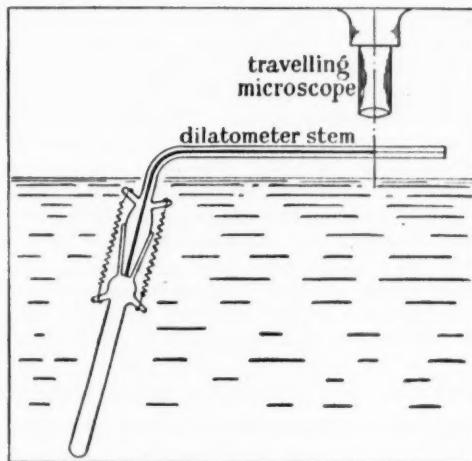


FIG. 1.—Sketch of dilatometer.

66 measured points taken consecutively during one day. Detailed calculations were also performed on runs 2 and 5, and gave on all accounts substantially equally good agreement. In particular, the results fitted the statistical law better than a first-order equation.

The acid latex was stored in a dropping funnel at -20°C in a frozen condition. When required for filling the dilatometer, it was allowed to attain about $+10^{\circ}\text{C}$, stirred and evacuated to 1 inch of mercury for about 10 minutes. The evacuation was found essential to avoid the evolution of a small amount of gas during the dilatometric run. The dilatometer was filled and weighed, thus giving the initial density D_0^L of the latex. Simultaneously, a sample was drawn for titration of the acid content by alkali, and one flocculated for the determination in a diffusion gradient tube of the density D_0^P of the pure polymer phase at that instant. The weight percentage of rubber in the latex was slightly variable from run to run, owing to creaming effects of the heavy sulfuric acid phase on the light rubber phase. The effect of this on the overall composition of the large remaining latex bulk was negligible. The correct rubber content of the latex in the dilatometer was calculated in two different ways, on the assumption that creaming did not disturb the kinetically significant concentration $c(\text{H}_2\text{SO}_4 / (\text{H}_2\text{SO}_4 + \text{H}_2\text{O}))$ of the acid. The first calculation was based on D_0^L and D_0^P the second on the acid titration. Close agreement between the two values ob-

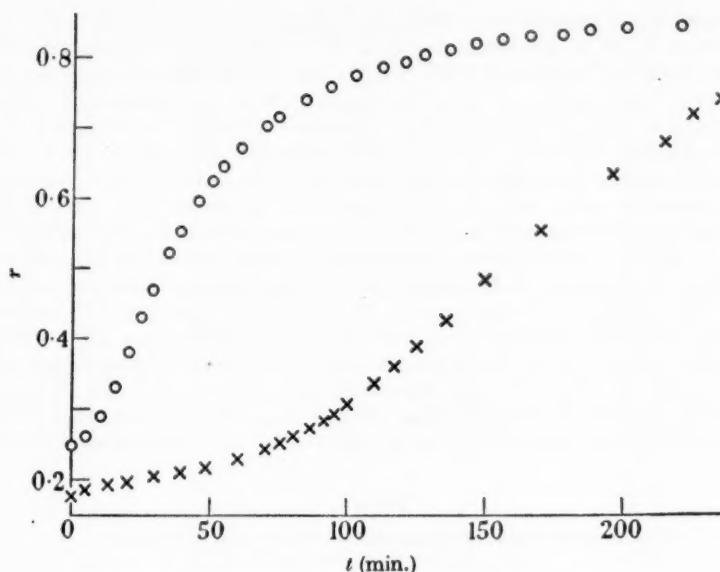
TABLE I

Run no.	Temperature ($^{\circ}\text{K}$)	Percentage concentration c of H_2SO_4	Rate constant k_1 (min. $^{-1}$)
1	298.5	78.1	0.00021
2	332.7	78.1	0.01732
3	338.5	78.1	0.02652
4	357.2	70.9	0.013
5	298.5	79.2	0.0002985
	298.5 corrected to 78.1		0.000192

tained justified the assumption just mentioned, and the value based on the titration was accepted. The dilatometer was immersed in the thermostat and 6 minutes allowed for thermal equilibration. The initial zero reading of the latex meniscus in the stem was then taken. The density D_0^P of the polymer at this instant was still close to D_0^P , the small change during equilibration being readily estimated from the subsequent rate. The isothermal contraction during the run was followed by noting the meniscus displacement M (cm.) from its original zero position to its final M_f . The total volume contraction during cyclization being less than 2 per cent, no stem correction was necessary for the cold latex drawn from the dilatometer stem into the dilatometer during the run. The omission of this very small and uncertain correction favors a first-order law over the statistical one, since it must cause a drop in the apparent reaction order. Curves showing the reaction progress r against time t are plotted in Figure 2. For this purpose r was calculated from the linear relation (21) linking it with M . Table 3 gives all the observed values of M and t for run 3.

CHECK ON THE VALIDITY OF THE TECHNIQUE

The rate constants of the dilatometric runs 2, 3 and 4 agree within a factor of two to three with the previous work based on measurement of D^P in a gradient tube. This would be accounted for by an error of about 2 per cent in

FIG. 2.—Plot of degree of cyclization r against t minutes. \circ , run 3; \times , run 4.

the sulfuric acid concentration c , but agreement is actually somewhat better, because the present rate constants k_s refer to the statistical law and take cognizance of the induction period⁹, while the previous work employed first-order constants k_1 . The much less satisfactory agreement of the k_s values for the runs at 25.3° C with the previous rate constants reflects a lower activation energy than previously found, a discrepancy discussed later⁹.

As an independent check on the validity of the present method the total measured volume contraction was calculated from M_f and compared with the separately measured density change of the polymer phase proper. To this end the practically stationary final density D_f^P of the polymer was measured in a gradient tube at the end of the run, and D_i^P calculated from M_f for compari-

TABLE 2
DETAILS OF MEASUREMENTS FOR RUN 3

Immersed volume of dilatometer	V	= 3.754 ₂
Rate of meniscus movement with latex volume	dM/dV^L	= 128.7 cm. ⁻²
Initial density of latex at 25° C	D_i^L	= 1.4985 g./cc.
Rubber content calculated from compounding, by weight		19.1%
Actual accepted rubber content (see text)		16.3%
Mean mass of rubber in V during run (calc. at 25° C)	m	= 0.926 g.
Observed final meniscus displacement	M_f	= 9.45 cm.
Density of (slightly cyclized) starting polymer (25° C)	D_0^P	= 0.920 ± 0.001
Estimated polymer density at first meniscus reading (25° C)	D_i^P	= 0.922 ± 0.002
D_i^P calculated from Formula (18) as a check		= 0.920 ₄
Final density of cyclized polymer (25° C)	D_f^P	= 0.981 ₃
Mean apparent coefficients of cubical expansion measured:		
H_2SO_4 (79%)		= 0.000551 ° C ⁻¹
Initial latex (slightly cyclized)	C_i^L	= 0.00053 ₇ ° C ⁻¹
Final latex (fully cyclized)	C_f^L	= 0.00046 ° C ⁻¹

son with the measured value (i.e., the corrected value based on D_0^P). As shown in Table 2, D_i^P calculated from M_i according to Formula (18) was 0.9204, while D_0^P was found 0.920 ± 0.001 and D_i^P estimated therefrom 0.922 ± 0.002 . This agreement shows satisfactorily that the dilatometric volume change of the latex reflects the volume change of the rubber particles in it during cyclization, especially if it is borne in mind that small effects due to non-rubber components in the latex have been neglected and that a large number of measurements enter into the calculation. In particular, the dilatometric volume change being measured at $65.3^\circ C$, but the polymer densities at $25.3^\circ C$ ($\Delta T = 40^\circ C$), a correction was required for the difference of the apparent coefficients of expansion of the initial latex C_i^L and the final latex C_f^L . Thus since the coefficient of expansion of the starting polymer (slightly cyclized rubber) was about 0.0005, but that of the fully cyclized rubber about 0.0002 only, the volume contraction of the latex at $65^\circ C$ was about 16 per cent larger than at $25^\circ C$. The C^L values were measured in the same dilatometer over the same range T , so that disturbing effects such as the small expansion of the Pyrex dilatometer itself could be neglected. All the measurements are re-

TABLE 3
DISCRIMINATION BETWEEN FIRST-ORDER AND STATISTICAL
CYCLIZATION KINETICS

Point no.	Meniscus displacement M (cm.)	Time (min.)		
		$t_{\text{obs.}}$	t_{c} calc.	scale
0	0.0	0	11.51	9.81
1	0.148	4	12.12	10.51
2	0.220	5	12.39	10.85
3	0.315	6	12.78	11.31
4	0.562	9	13.81	12.51
5	0.655	10	14.19	12.97
6	0.761	11	14.68	13.51
7	1.002	13	15.74	14.75
8	1.134	14	16.33	15.45
9	1.270	15	16.97	16.17
10	1.407	16	17.62	16.92
11	1.714	18	19.16	18.65
12	1.865	19	19.95	19.53
13	2.020	20	20.76	20.44
14	2.324	22	22.45	22.31
15	2.588	24	23.98	24.00
16	2.777	25	25.14	25.25
17	3.064	27	26.97	27.22
18	3.195	28	27.84	28.15
19	3.338	29	28.84	29.38
20	3.871	33	32.80	33.31
21	4.126	35	34.87	35.44
22	4.344	37	36.77	37.36
23	4.571	39	38.84	39.43
24	4.765	41	40.75	41.29
25	4.949	43	42.63	43.14
26	5.226	46	45.65	46.09
27	5.407	48	47.79	48.13
28	5.649	51	50.87	51.02
29	5.806	53	53.00	53.02
30	5.968	55	55.33	55.16
31	6.166	58	58.39	57.96

TABLE 3—Continued

Point no.	Meniscus displacement M (cm.)	Time (min.)		
		$t_{\text{obs.}}$	$t_{\text{calc.}}$	$t_{\text{scale.}}$
32	6.351	61	61.46	60.76
33	6.541	64	64.87	63.81
34	6.706	67	68.06	66.68
35	6.841	70	70.94	69.17
36	7.018	74	74.93	72.68
37	7.177	78	78.87	76.12
38	7.390	84	84.80	81.20
39	7.675	93	94.11	89.10
40	7.777	97	97.91	92.36
41	7.900	102	102.93	96.62
42	8.018	107	108.29	101.17
43	8.096	112	112.15	104.47
44	8.192	117	117.32	108.91
45	8.229	120	119.47	110.75
46	8.302	124	124.02	114.68
47	8.347	127	127.00	117.25
48	8.403	131	130.91	120.73
49	8.464	136	135.54	124.89
50	8.543	141	142.24	130.96
51	8.558	145	143.54	132.27
52	8.613	149	148.89	137.20
53	8.681	155	156.21	144.27
54	8.721	159	160.84	149.08
55	8.723	162	161.22	149.35
56	8.761	165	165.98	154.50
57	8.772	168	167.39	155.98
58	8.804	172	173.44	161.10
59	8.838	177	177.43	167.38
60	8.879	187	184.36	176.08
61	8.916	192	191.45	186.36
62	8.954	200	199.58	200.00
63	8.962	205	201.73	203.45
64	9.007	220	213.49	231.63
65	9.349	316	∞	∞
66	9.450	393	∞	∞

corded in Table 2 and the formula employed was

$$1/D_i^P = 1/D_f^P - M_f - \frac{\Delta TVdM/dV(C_i^L - C_f^L)}{m(dM/dV)} \quad (18)$$

On the assumption that the deprotonation step in (1) is rate determining, an upper limit previously estimated for the basic strength of rubber (pK_a of the carbonium ion III < about -8) is here experimentally confirmed. Thus since the volume change during cyclization must be associated very largely with the proton transfer step which precedes the slow deprotonation, the protonation and transfer equilibria in (1) cannot lie more than a few per cent over the products, otherwise the slow contraction observed on the latex would correspondingly fall short of the contraction of the rubber phase during cyclization.

DISCRIMINATION BETWEEN STATISTICAL KINETIC AND FIRST-ORDER LAW

It will now be shown that the main central portion of run 3, covering about 78 per cent of the measured volume change and 50 per cent of the total cyclization reaction, conforms definitely to the statistical Equation (19), with $F(r)$

as defined in (13), rather than to the first-order law (20). The comparison is exhibited in Table 3 by confronting the observed times $t_{\text{obs.}}$ with times t_s calculated from (19) and t_1 calculated from (20):

$$k_s i_s = F(r) - F(r_i) + x \quad (19)$$

where

$$r_i = 0.2468 \quad F(r_i) = 0.3052 \quad x = 0.3052 \quad k_s = 0.02652 \text{ min.}^{-1}$$

$$k_1 t_1 = -\log(1 - r) + \log(1 - r_i) + x' \quad (20)$$

where

$$r_i = 0.1879 \quad -\log(1 - r_i) = 0.7261, \quad x' = 0.7368, \quad k_1 = 0.010307 \text{ min.}^{-1}$$

The calculation of the times and of the r 's are respectively slightly complicated because a small initial portion of all the runs and a very small final portion of the runs at elevated temperature conformed with neither law. Thus in fitting the experimental $t_{\text{obs.}}$ and the r values calculated from the measured meniscus displacements M to Equations (19) and (20), ideally only the rate constants k_s and k_1 require adjustment. In practice, however, two small additional adjustments have to be made in both cases to allow for the initial and final deviations. These adjustments do not conceal any favored treatment of either law. Thus the first adjustment concerns a displacement of the time origin by an amount x or x' , respectively, as shown in the last two equations, to allow for an induction period, which is visible in Figure 2 and whose significance is discussed⁹. Probably fortuitously, these adjustments cancelled the integration constants $F(r_i)$ and $\log(1 - r_i)$ in runs two and three within experimental error, so that the main part of the reaction proceeded along the theoretical curve for $r_i = 0$ and absence of an induction period.

The meniscus movement reflecting accurately¹⁰ the volume change in the rubber phase is, therefore, linearly related to the reaction progress:

$$aM = r - r_i \quad (21)$$

where for Equation (19), $a = 0.0669$, $r_i = 0.2468$; and for Equation (20), $a = 0.0897$, $r_i = 0.1879$. Ideally, the constant a should be fixed as $(r_f - r_i)/M_f$. However, the abnormality at the end of the reaction⁹ causes a slow volume change after (on the kinetic evidence) cyclization is complete, and thereby affects M_f and a . For Equation (19), $r_f = 0.8647$ and $(r_f - r_i)/M_f = 0.0654$, while 0.0669 gives the best fit. Again, for Equation (20) $r_f = 1$, the theoretical $a = 0.08593$, while $a = 0.0897$ gives the best agreement. The r_i values chosen correspond closely to those calculated from D_s^P and the density (0.900) of uncyclized rubber. It is emphasized that after suitable adjustments in a and k_s (but not k_1), variations in the assumed r_i of ± 0.1 leave the fit of equation (19) practically, and that of Equation (20) exactly, unaltered, because of an invariant property of the first order law. Table 3 lists the times $t_{\text{obs.}}$, and the times t_s and t_1 , respectively calculated from Equations (19) and (20), with the aid of (21).

After an induction period of about 20 minutes, 28 out of 49 consecutive values of t_s , covering an interval of 180 minutes, lie within 30 seconds of the experimental $t_{\text{obs.}}$, 12 points lie between $\frac{1}{2}$ and 1 minute, 8 points between 1 and 2 minutes, and only one point between 2 and 3 minutes off. On the other hand, the t_1 values, while agreeing about equally well over the range from 20 to 70 minutes, and again at 200 minutes, deviate between 70 and 200 minutes

smoothly up to a maximum of over 12 minutes from the t_{obs} . These facts show not only that a conclusive experimental decision in favor of the statistical law (19) has been obtained, but also the high accuracy actually required for such a decision.

DEPENDENCE OF RATE ON ACIDITY AND TEMPERATURE

The usual Arrhenius plot of the runs listed in Table 1 is shown in Figure 3. The best straight line through runs 1, 2, 3 and 5 has been drawn, and from this the rate at 357.26° K and sulfuric acid concentration $c = 78.1$ per cent can be computed. When this is compared with run 4, at the same temperature but

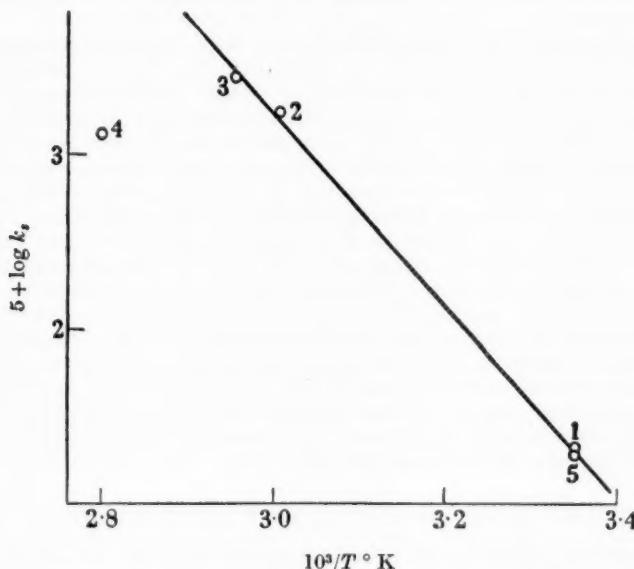


FIG. 3.—Arrhenius plot for runs 1 to 5. (For numbering *cf.* Table 1.)

at $c = 70.9$ per cent the relation:

$$\frac{d \log k_r}{dc} = 0.165 \quad (22)$$

is found between these two concentrations, in very good agreement with the value (0.17) obtained in the previous work, so that the correlation between reaction rate and Hammett's acidity function⁶ H_0 is confirmed. The small correction of the rate of run 5, from the measured value at $c = 79.23$ to the desired value at $c = 78.1$, as shown in Table 1, is based on Equation (22).

The temperature dependence of the rate of cyclization agrees much less well with that previously reported, the activation energy calculated from runs 1, 2, 3 and 5 being 25.3 kcalories instead of 32.7, and the frequency factor 4×10^{14} min.⁻¹ instead of 3×10^{19} . The main reason for these deviations must be

sought in the runs at 25.3° C, which showed much higher rates than predicted from the previous work. Two explanations may be advanced for these deviations. First, while the overall activation energy of 32.7 kcalories previously found referred to a temperature range between 25 and 100° C, the Arrhenius plots showed some definite curvature, and lower values can be calculated from the data falling within the range 25 to 65° C here studied. Thus the three points in the earlier work at 78.5 per cent acid in this temperature range correspond to 29.8 kcalories the two points at 72.6 per cent acid to 24.8 kcalories of activation energy. Secondly, the previous density technique was based on the assumption of a unimolecular law and was insufficiently sensitive to show the initial and final rate abnormalities observed in this work⁹, and is accordingly regarded as less reliable in the calculations of the Arrhenius parameters of the cyclization step.

The only serious implication of the lowering of the Arrhenius parameters at 78.1 per cent acid and between 25 and 65° C which has thus been accepted is a weakening of the support previously derived from the exalted frequency factor for the rate control by the deprotonation step (as in scheme (1)) rather than by the first (protonation) step. It has been shown⁴ that a very high-frequency factor such as 10^{19} min.⁻¹ could correlate only with a reaction step in which ionic charges were neutralized in the transition state, *e.g.*, a collision between the cyclocarbonium ion III and an HSO_4^- -ion to produce IV and H_2SO_4 . The new value of 4×10^{14} is now normal for a unimolecular reaction, though still very high for a collision between an ion and a large uncharged molecule, such as occurs in the protonation step. Moreover, from the previous experience cited, the frequency factor may be expected to rise with temperature, and certainly with acid concentration *c*, so that considerably higher values could actually be experimentally realized. Since the deprotonation rate control is by no means an unusual mechanistic feature, and has been supported also by the influence of the structure of various terpene substrates on their approximately known cyclization rates, it is still the preferred mechanism though on weaker grounds in view of the reduced activation entropy.

SMALL INITIAL AND FINAL RATE ABNORMALITIES

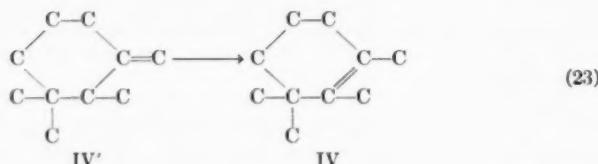
An induction period of reduced rate was observed in the runs at elevated temperature. While, as Figure 1 shows, this was particularly marked at the reduced acidity of run 4, it did not interfere even there with the determination of the rate constant of the later regular part of the reaction. Trials showed that the detailed course of this induction period was accurately reproducible for a given latex. As at 25° C the initial rate abnormality was much reduced in importance relative to the main change, it follows that whatever the mechanism responsible for it, it must be subject to a much smaller activation energy. The abnormal rate period split into two phases at 25° C. The first phase on bringing the latex from a low temperature to 25° C and equilibrating, was a burst of volume contraction, lasting for about 100 minutes at first several times too fast compared with the later regular reaction. This slowly died down to a rate below the normal value and then rose back to the normal in a few hours. These effects were likewise reproducible and confined to the first 10 to 20 per cent of the total measured contraction. Whether the burst occurred also at elevated temperature is uncertain, as it would there be obscured by the time of equilibration of temperature, though it is visible in the slow run (Figure 1). Its sig-

nificance is not understood, and it may indeed be connected with some side reaction in the complex colloidal latex system, rather than with cyclization. The induction period of reduced rate may be connected with the rate of diffusion of the acid catalyst into the rubber particles¹¹, a conclusion supported by its low activation energy.

Detailed consideration shows that the small induction period cannot reasonably be accounted for by any chain-reaction mechanism for cyclization. The most plausible chain mechanism would have the effect of cyclization of a couple of isoprene units spread to an adjacent couple, and so on all along the segment of chain remaining uncyclized. This mechanism would arise, for instance, if the deprotonation step of one ring became the protonation step of the adjacent unit. Such a scheme would bear only superficial resemblance to the acid-catalyzed chain polymerization of olefins, though a number of radical reactions of rubber have been formulated as similar chain sequences of cyclizations involving two units at a time¹². The correlation of cyclization rate with Hammett's acidity function H_0 indicates a proton transfer from the acid to the rubber; this step would actually have to be rate controlling in any chain mechanism, as the alternative of deprotonation control (as in (1)) would not be available. A chain mechanism controlled by the activating protonation would, however, have a higher reaction order than here observed, indeed as high as two under the simplest assumptions. This will be appreciated from the simple argument that at half-cyclization ($r = 0.5$), the rate of cyclization would, compared with the starting rate, be halved because the number of units available for activation would be halved, and then again be halved because each activation would, on average, lead to the rapid cyclization of chains of only half the original length. Thus it does not appear possible that any chain mechanism would produce rate equations that could approach the excellent agreement with experiment achieved by the nonchain mechanism (1) and Equation (19). Moreover, the number of widowed units in a chain mechanism would fall to a much smaller proportion than the 13.5 per cent of Flory's theory for a nonchain mechanism, which is in close agreement with Fisher and McColm's analytical results on cyclized rubber⁵.

Turning now to the rate abnormalities at the end of the reaction, these reflect a step subsequent to cyclization proper, since the density of the rubber increases gradually well above the end point approached kinetically during the main part of the reaction. At the highest temperatures previously employed (90 to 100° C), at which there is some danger of oxidative side reactions, densities up to 0.990 had been recorded. It has since been found that at $c = 78$ per cent and 60° C ten different latexes gave definite end products, whose densities lay between 0.984 and 0.985, even after several hours' continued maintenance under these reaction conditions. The reproducibility of this cyclized rubber must be regarded as high, since most synthetic polymers are sold commercially on density specifications to the second decimal place only. The polymer density approached by the main part of the reaction in the high-temperature dilatometer runs was near to 0.980. The nature of the subsequent shift to 0.984-5, which took several hours to complete, might be sought in a cross linking or in a prototropic displacement of the remaining double bonds. The latter alternative seems more likely, since there appears to be no marked decrease in solubility or swellability. There is some intrinsic probability that the thermodynamically less stable γ -terpene from IV' is formed first, and the subsequent reaction might thus be its transformation to the

β -form IV:

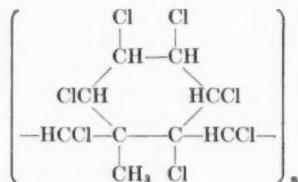


Some spectroscopic evidence has been quoted earlier¹¹ for the presence of rings IV' in cyclized rubber, though a detailed confirmation of the reaction (23) will require further spectroscopic examinations to be made. (23) would account, not only for the small volume decrease found, but also for the marked rise in softening point, because the semicyclic double bond would confer mobility on the ring IV', while the endocyclic bond in IV would cause considerable stiffening.

In the runs at 25° C the reaction was too slow to carry the polymer in practice beyond a density of 0.974.

CONCLUSIONS

The emulsion technique of making kinetic measurements on latex rubber, presents, among other advantages, much higher precision than earlier methods. The average reaction order of the present measurements being approximately 1.25, the convulsive discrimination from a 1.0 order law necessitated not only the highest attainable precision, but also a careful investigation¹² of the mathematical effects of possible errors in all the parameters involved. As an illustration of the difficulties of the earlier methods, the simple unaccelerated vulcanization of rubber with sulfur may be cited. Several investigators, working with bulk (as distinct from latex) rubber, assessed the order of this reaction at values ranging from zero to over 1. The correct value is undoubtedly unity, as shown by the analysis of adiabatic rate measurements¹⁴, in agreement with the most likely mechanism. The rate-determining step being the splitting of a sulfur ring without aid from the polymer, statistical kinetic effects are not encountered in vulcanization. Numerous examples of statistical kinetic and equilibrium effects probably do exist in rubber chemistry. Farmer¹⁵ described several reactions of other substances (SO₂, Cl₂, maleic anhydride) with two neighboring units of rubber at a time. Statistical effects should apply to all these at equilibrium through the survival of uncyclized units, and wherever, in the absence of chain mechanisms, rubber enters the rate-controlling step, Equation (13) may be expected to apply. As an example, the empirical formula (C₁₀H₁₁Cl₇)_n has been accepted by Le Bras and Delalande¹⁶ in support of the structure



which is closely analogous to IV. Uncyclized units, probably $\text{HCl}-\text{CCl}-\text{CHCl}-\text{CHCl}$, should accompany these rings, in amounts varying from 13.5 per cent down to negligible proportions, since the kinetic chain varies in length from units (single cyclization act without lateral propagation) to large numbers. The diagnostic value in studies of reaction mechanism of the appropriate statistical analysis is thus evident, though the experimentally attainable precision is here still the limiting factor.

The present work has confirmed the postulated mechanism by its demonstration that the rubber polymer enters the rate-determining step in cyclization. It has established that this reaction is essentially not an intermolecular cross-linking, but a reaction between couples of neighboring units in a long chain, 13.5 per cent of which escape from cyclization. Indeed, a purely kinetic proof has now been furnished of the basic fact that rubber is a polymer, containing long chains of identical units.

SUMMARY

Rubber cyclization provides a useful illustration of statistical effects intervening in the reactions of long-chain polymers. Analogously to the known cyclizations of simple diisoprenic terpenes, each individual cyclization act links two adjacent isoprene units in the rubber chain into a six-membered ring. However, some of the units remain stranded between neighboring rings and escape cyclization for want of a partner. Thus the final polymer has a copolymer structure of 86.5 per cent of diisoprenic rings and 13.5 per cent of uncyclized monisoprenic units. This result is derived from a statistical theory of Flory, and has previously found accurate experimental verification. The bearing of this statistical effect on the reaction kinetics has now been studied for the first time. Dilatometric experiments on rubber emulsions in sulfuric acid have shown that the cyclization reaction conforms in the main with a statistical cyclization law much better than with a first-order equation uncorrected for the survival of stranded units. High accuracy was required for this experimental distinction, whose importance lies in the implicit proof that the polymer units participate in the rate-determining transition complex, in accordance with the accepted proton transfer mechanism. A kinetic proof has incidentally been furnished for the fact that the rubber polymer contains long chains of identical units. When handled by an emulsion technique, this polymer can provide a useful "model compound" for its simpler terpene analogs.

Certain rate abnormalities have been observed, including an induction period of reduced rate, probably connected with diffusion effects. A small volume change subsequent to the cyclization reaction may reflect a prototropic double-bond shift. The activation energy and entropy are found to be lower than in previous work, an effect traced in part to a curvature of the Arrhenius plot. The known dependence of cyclization rate on Hammett's acidity function H_0 is quantitatively confirmed.

ACKNOWLEDGMENT

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- ⁹ See section on SMALL INITIAL AND FINAL RATE ABNORMALITIES.
- ¹⁰ See section designated EXPERIMENTAL.
- ¹¹ Gordon, "Hevea Rubber. Cyclization kinetics and proton affinity," Thesis, London University, 1949.
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CHANGES OF THE MECHANICAL PROPERTIES OF VULCANIZATES DURING THE EARLY STAGES OF THERMAL OXIDATION *

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We have already devoted a number of works¹ to the study of the mechanism of oxidation of various types of polymers, and have shown in these investigations that the processes of inhibited and autocatalytic oxidation proceed at different rates, possess different temperature coefficients of rate, and can in no way be identified. The oxidation process is accompanied at all stages by profound structural changes of permanent character, leading ultimately during autocatalysis to complete loss of the valuable technical properties of rubbers. One study was dedicated to the changes of mechanical properties of vulcanizates of various rubbers during inhibited and autocatalytic oxidation. This study was particularly useful because many authors², disregarding the difference between the inhibited process and freely developing autocatalytic oxidation, introduced much misunderstanding into the general problem of the oxidation of rubbers.

EXPERIMENTAL PART

In order to reduce to a minimum the influence of the different ingredients in a rubber mixture on the progress of the oxidation process, we used unloaded vulcanizates, with tetramethylthiuram disulfide as the vulcanizing agent. The recipe had the following composition (in parts by weight per 100 parts by weight of rubber):

Rubber	100
Tetramethylthiuram disulfide	3
Stearic acid	1
Zinc oxide	1
Phenyl- β -naphthylamine	0.5

All the rubbers studied were highly purified before the mixtures were prepared. They were purified twice: first, by extraction by an azeotropic mixture (80 per cent acetone and 20 per cent methanol) in a cold atmosphere of pure nitrogen, and then precipitation with chemically pure methanol from 3 per cent benzene solution. The precipitated rubbers were dried in *vacuo* (10^{-8} mm. mercury) at room temperature to constant weight.

The rubbers thus dried were mixed with the compounding ingredients on a laboratory micromill (1:1.15). From the mixtures obtained, 2 per cent benzene solutions were prepared. Sheets were made from the benzene solutions on cellophane, and spread on special molds. The molds were filled with the solution so as to obtain sheets of 100–120 μ thickness.

The sheets were vulcanized at 143° C according to the method described by

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Kolloidn^I Zhurnal*, Vol. 14, No. 1, pages 40–45 (1952).

one of the authors³. The optimum vulcanization for sodium-butadiene rubber was 90 minutes, for polybutadiene and natural rubbers, 60 minutes.

STRUCTURAL MECHANICAL CHANGES OF VULCANIZED NATURAL RUBBERS

Figure 1 gives data for the structural-mechanical changes of vulcanizates during the induction period of oxidation and at the beginning of autocatalysis. The initial concentration of inhibitor was 0.5 per cent; the temperature of oxidation, 90°; and the duration of the induction period, 70 hours.

As is seen from Figure 1, decreases of tensile strength, modulus, and relative elongation are observed at the beginning of the induction period; these factors then remain constant till near the end of the induction period. The transition from induction to autocatalysis is characterized by a sharp increase of the rate of oxidation, immediately affecting the physical-mechanical properties of the vulcanizates. As soon as the induction period is terminated, complete loss of

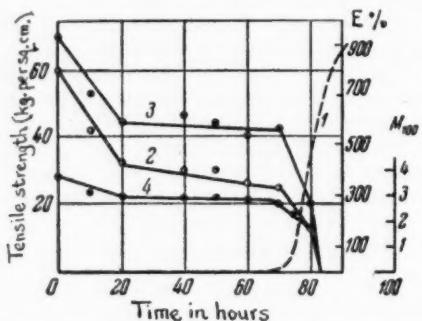


FIG. 1.—Relation of mechanical properties of vulcanized natural rubbers to the time of oxidation in the initial period.

1. Oxidation.
2. Tensile strength in kg. per sq. cm.
3. Relative elongation E in percentage.
4. Modulus M_{100} in kg. per sq. cm.

the original properties of the rubber is observed; the vulcanized high elastic materials are transformed into sticky flowing masses.

STRUCTURAL-MECHANICAL CHANGES OF VULCANIZATES OF POLYBUTADIENE-STYRENE RUBBER

Figures 2 and 3 present data on the structural-mechanical changes of vulcanizates in the induction period of oxidation, with an initial inhibitor concentration of 0.5 per cent.

Calculated on the butadiene component, polybutadiene-styrene rubber contains 35 per cent of double bonds in the main chains and 65 per cent in the side chains. The data of Figures 2 and 3 indicate the presence of two processes: structure formation and disintegration. Whereas at an oxidation temperature of 90° C. the vulcanizates develop structure formation, at an increased temperature (133° C.) oxidation degradation begins to prevail over structure formation, there is a decrease of modulus and of tensile strength at almost constant relative elongation.

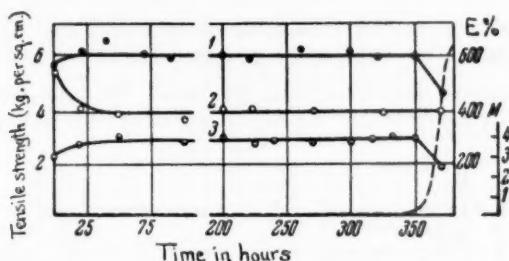


FIG. 2.—Relation of mechanical properties of polybutadiene rubber to time of oxidation in induction period; temperature of oxidation 90°.

1. Tensile strength in kg. per sq. cm.
2. Relative elongation E in percentage.
3. Modulus M in kg. per sq. cm.

STRUCTURAL-MECHANICAL CHANGES OF VULCANIZED SODIUM-BUTADIENE RUBBER

Figures 4 and 5 present data on the structural-mechanical changes of vulcanizates during the induction period of oxidation. In this induction period of oxidation, the processes of structure formation (increase of modulus and tensile strength) predominate, and the intensity of these changes increases with increase of temperature.

INFLUENCE OF INITIAL CONCENTRATION OF INHIBITOR ON STRUCTURAL CHANGES OF VULCANIZED SODIUM-BUTADIENE RUBBERS

Figure 6 shows data on the influence of the initial concentration of inhibitor on the structural-mechanical changes of vulcanizates in the induction period of oxidation. The oxidation temperature was 133° C. The initial concentration of inhibitor and the range of 0.25–0.5 per cent concentration has practically no influence on the rate of structural-mechanical changes.

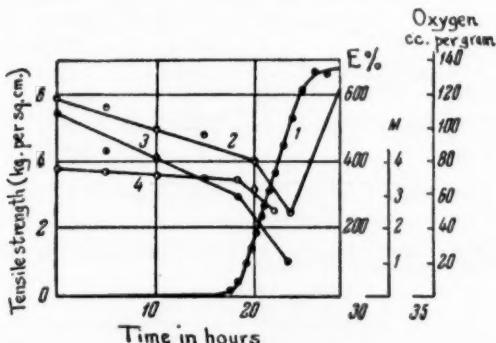


FIG. 3.—Relation of mechanical properties of vulcanizates of butadiene-styrene rubber to time of oxidation in its induction period; temperature of oxidation 133° C.

1. Oxidation (O_2) in cc. per g.
2. Tensile strength in kg. per sq. cm.
3. Relative elongation E in percentage.
4. Modulus M in kg. per sq. cm.

EFFECT OF INITIAL CONCENTRATION OF INHIBITOR ON THE "WORK CAPACITY" OF VULCANIZED BUTADIENE-STYRENE RUBBER

The experimental data are given in the table. The temperature was 22°; deformation rate 250 cycles per minute; amplitude of deformation 50 per cent.

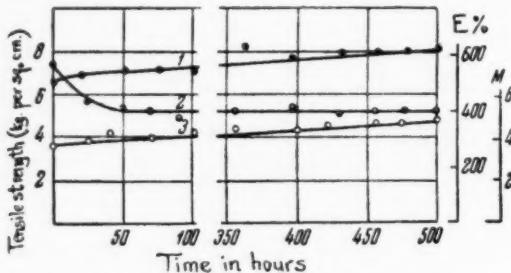


FIG. 4.—Relation of mechanical properties of vulcanized sodium-butadiene rubber to time of oxidation in the induction period; oxidation temperature 90°C.

1. Tensile strength in kg. per sq. cm.
2. Relative elongation E in percentage.
3. Modulus M in kg. per sq. cm.

As is seen from Table 1, the "work capacity" of vulcanizates largely depends on the concentration of inhibitor.

INTERPRETATION OF RESULTS

The results given in the experimental part show that the physical-mechanical properties of vulcanizates always change during the induction period of oxida-

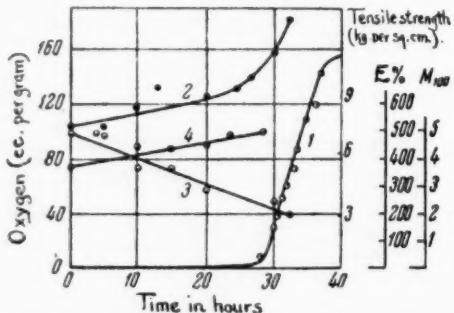


FIG. 5.—Relation of mechanical properties of vulcanized sodium-butadiene rubbers to time of oxidation in the induction period; temperature of oxidation 133°C.

1. Oxidation (O_2) in cc. per gram.
2. Tensile strength and kg. per cc.
3. Relative elongation E in percentage.
4. Modulus M_{100} in kg. per sq. cm.

tion. The transition from the induction period to autocatalytic oxidation leads to a radical change of the mechanical properties of all vulcanizates. These changes become more conspicuous as the induction period of oxidation becomes shorter. Such a sharp change of mechanical properties is due pri-

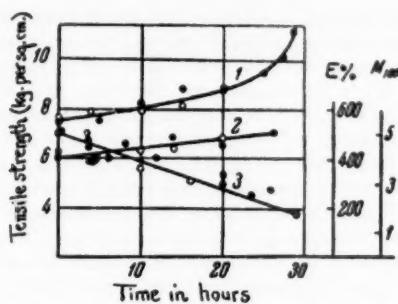


FIG. 6.—Effect of the initial concentration of inhibitor on the changes of mechanical properties of vulcanizates of sodium-butadiene rubbers in the induction period of oxidation.

1. Tensile strength in kg. per sq. cm.
2. Modulus M_{100} in kg. per sq. cm.
3. Relative elongation in per cent.
4. Concentration of inhibitor:
 - 0.25% in rubber
 - 0.50% in rubber

marily to the large increase of the rate of oxidation. However, the difference here is not only quantitative but also qualitative. The accumulation of a large quantity of polar groups in autocatalysis results in a large increase of intermolecular activity, and also leads to secondary reactions between these groups, particularly to the formation of ether bridge bonds.

For the majority of rubbers known, these structural changes of the induction period proceed at constant rates. For this reason the total change of the physical-mechanical properties of rubbers in the kinetic zone depends on the time period.

It is interesting to consider the principles of the structural changes in inhibited and autocatalytic oxidation. Certain investigators consider the formation of ether bonds in oxidized rubber a basic cause of structure formation. Our own experiments, which were especially designed to detect ether groups in vulcanizates of sodium-butadiene rubber oxidized before the beginning of the induction period, showed that the formation of ethers in this kinetic stage of oxidation is not appreciable.

Comparing the data for the structural changes of vulcanizates of sodium-butadiene and butadiene-styrene rubbers at the oxidation temperature 133°C , it is clear that the rate of these changes in vulcanized sodium-butadiene rubber is much greater than in butadiene-styrene rubber. The rates of oxidation of both these vulcanizates are, however, the reverse. It is known that the rate of inhibited oxidation of butadiene-styrene rubber is 3 times greater than that of sodium-butadiene rubber. At an oxidation temperature lower than 100°C , the structural changes in both vulcanizates take place at roughly the same rate.

TABLE I

RELATION OF WORK CAPACITY OF VULCANIZATES OF BUTADIENE-STYRENE RUBBER AND ORIGINAL CONCENTRATION OF INHIBITOR

Concentration of inhibitor in %	Work capacity in hours	Work capacity in 1000 cycles
0.25	7.5	113.0
0.50	13.0	198.0
1.00	17.0	255.0

The existence of an inverse relation between the rate of oxidation and rate of change of mechanical properties of the two given vulcanizates leads us to believe that the structural changes are caused, not only by oxidation, but also by other factors. Work by Kuzminskii, Shokhin, and Belitzkaya⁴ indicated that the double bonds of the side chains, which do not take part in the initiation of the oxidation processes, cause a thermal structure formation in butadiene polymers. It is evident that the specific effects of these processes at oxidation temperatures above 100° C are quite large: the greater the content of double bonds in the side chains of the polymer, the more extensive is the process of structure formation. In fact, in sodium-butadiene rubber containing 80 per cent of its double bonds in the side chains, the processes of structure formation predominate. For natural rubber, in which all the double bonds are located in the main chains, degradation by oxidation predominates. Consequently structure formation must be related to oxidation, which takes place not only at the double bonds of the main chains, but also at those in the side chains. Naturally the changes of mechanical properties of vulcanizates during inhibited oxidation reflect the entire complex of transformations which cause the thermal structure formation, as well as oxidation, *i.e.*, degradation and polymerization.

As was observed above, the physical-mechanical properties of vulcanizates are in a continuous state of change, even in the induction period of oxidation. The processes which take place in the induction period of oxidation of vulcanizates can be reduced to two: (1) the formation of primary active oxygen-bearing centers (initiation of the process), and (2) reaction of the latter with phenyl- β -naphthylamine, leading to rupture of the oxidizing chains on the first link. Such a theory does not exclude the possibility of decomposition of a certain quantity of active peroxides before reaction with the inhibitor. Decomposition of the active peroxides leads inevitably to rupture of the molecular chains of the rubber and this is the first stage of the change of the physical-mechanical properties of the latter. Naturally, an increase of the equilibrium concentration of active peroxides (primary active centers) increases the probability of their spontaneous decomposition.

From the equation of state (inhibited oxidation):

$$W_i = - \frac{db}{dt} = K_i [C][O_2] = K_c [b][n_0]$$

it follows that:

$$[n_0] = \frac{K_i}{K_c} \cdot \frac{[C][O_2]}{[b]} \quad (1)$$

Here W_i is the rate of oxidation, $[C]$ is the concentration of double bonds in the polymer; $[O_2]$ is the concentration of oxygen; K_i is the initiation constant; K_c is the constant of rate of reaction of the inhibitor with the active peroxides; $[b]$ is the concentration of inhibitor, and $[n_0]$ is the concentration of primary active centers (active peroxides).

Since $[C]$ and $[O_2]$ hardly change under the conditions of inhibited oxidation and can be assumed to be practically constant, it follows from Equation 1 that the value of $[n_0]$ is determined by the values of K_i , K_c , and $[b]$. It is known that K_i characterizes the reactivity of the rubber and K_c the activity of the inhibitor. It should be noted that, with an increase of temperature, K_i increases faster than K_c , since the energy barrier of the reaction of oxygen with rubber is 22.5 kcal. per mole, and of an active peroxide with inhibitor only 6-7 kcal. per mole.

By virtue of the reasons cited above, with an increase of temperature the probability of decomposition of the peroxides before the reaction with the inhibitor increases; this is immediately reflected in the mechanical properties of the vulcanizates.

As would follow from Equation (1), the rate of change of the mechanical properties of vulcanizates must depend also on the amount of inhibitor added. However, in reality no such relation was observed (see Figure 6). This can be explained by the presence in the vulcanizates of a large excess of inhibitor, even in the smallest concentrations, in comparison with the amount of primary active centers formed.

Thus it is clear that the change of mechanical properties of rubbers during a change of concentration of inhibitor is so small that it lies within the limits of experimental error. The influence of the concentration of inhibitor, however, appears to a large degree in the study of the swelling of vulcanizates (see Figure 5), where even slight changes of the mechanical properties cause a sharp change of their work capacity.

CONCLUSIONS

1. The structural-mechanical properties of vulcanizates of various rubbers during the time of the induction period and during autocatalytic oxidation were studied.

2. A change of the mechanical properties of vulcanizates in the induction period is a consequence of oxidation (degradation and polymerization) and thermal structure formation, taking place with the participation of the double bonds of the side chains.

3. In complete accord with the theory, at the end of the induction period and in the early stages of autocatalysis, the physical-mechanical properties of vulcanizates change sharply; as a result of this, the vulcanizates lose their technical value.

4. During the heat aging of rubber, the concentration of inhibitor within the range of 0.25–0.5 per cent has no effect on the rate of change of the physical-mechanical properties of vulcanizates, but has a strong influence on the work capacity of the latter.

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BREAKAGE OF CARBON-RUBBER NETWORKS BY APPLIED STRESS *

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Rubber is markedly stiffened by the incorporation of reinforcing fillers, and this aspect of reinforcement has received much attention. Most rubber technologists define stiffness or "modulus" as the stress at a given extension or compression. An important fact to be noted in considering the stiffness of reinforced rubber is that it can be softened drastically by the application of a prestress which exceeds the stress attained during measurement. This phenomenon was first described and studied in some detail by Mullins¹ and has since been investigated and discussed in some of its aspects by the authors². The work described in the present paper was undertaken to throw more light on the mechanism of reinforcement by a study of the changes which occur when the rubber is stressed. It was considered that there was a particular need for a method of quantitative description of the stress-strain properties of reinforced rubber which included the softening of the rubber by applied stress. It was hoped that this approach would promote a clearer understanding of the nature and strength of the attachments between carbon particles and rubber molecules and their role in reinforcement.

QUANTITATIVE DESCRIPTION OF STRESS-STRAIN PROPERTIES

The approximately linear relation in certain experimental conditions between the extension at an arbitrary stress and the magnitude of greater previously applied stresses which was obtained² for a limited range of prestresses and for one type of reinforcing black does not apply for prestresses much outside the range 5 to 100 kg. per sq. cm. This method of studying changes in the stiffness of reinforced rubber by considering the extension at an arbitrary stress and the obvious alternative technique of considering the stress at an arbitrary extension (modulus) have not been adopted in the present investigation. It was thought that a mathematical relation between stress and extension for pre-stressed specimens would be more useful, if it could be obtained so that the stiffness characteristics could be represented by parameters which are independent of the extension. The most promising way of achieving this appeared to be through a semiempirical solution of the problem which, if successful, should lead to valuable fundamental information.

To be generally successful, any empirical equation for the stress-strain curve of reinforced rubber must continue to apply as the concentration of reinforcing material in the rubber is reduced to zero. This means that in certain conditions it must approximate the equation for rubber that has not been reinforced. Theoretical treatments of the elasticity of cross-linked rubberlike polymers in-

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volving the statistics of long chain molecules have been made by Kuhn³, James and Guth⁴, Wall⁵, Treloar^{6,7} and Flory and Rehner⁸. Guth and James⁹, and later Wall⁵, who used a different method from that of Guth and James, derived the following relation between stress and extension:

$$F = G \left[\alpha - \frac{1}{\alpha^2} \right] \quad (1)$$

where F is the force per unit area of original cross-section; α is the extension ratio, *i.e.*, the ratio of the extended length to the initial length; and G is defined as the modulus. Treloar⁶ has drawn attention to the close similarity in the underlying concepts of Wall's and of Kuhn's theories and has shown that, when suitably modified in detail, Kuhn's model also leads to Equation 1. This formula for simple extension has also been derived by Flory and Rehner⁸ on the basis of a rather different model. The basic idea underlying these theories is the now generally accepted kinetic theory of rubber elasticity. According to this theory the elasticity of rubberlike materials arises from the thermal motion in a lateral direction of segments of long-chain molecules whose freedom of movement is restrained by a limited number of cross-links so that a three-dimensional network of interconnected chains is formed. According to the theoretical derivations of Equation 1, modulus G is given by the expression:

$$G = \beta U k T \quad (2)$$

where U is the number of chains, *i.e.*, segments between junction points—in unit volume and may be taken to equal the number of cross links; k is Boltzmann's constant; and T is the temperature in degrees absolute. In this equation the factor, β , has been introduced by Guth, James, and Mark¹⁰ because they consider that the process of network formation leads to a distribution differing from that corresponding to free chains. The precise value of β depends on the detailed structure of the network. For chains having an initial distribution of displacement lengths corresponding to that for free chains β becomes equal to unity and

$$G = U k T \quad (3)$$

Bartenev¹¹ has quite recently proposed a stress-strain relation which differs from previous theories:

$$F = E \left[1 - \frac{1}{\alpha} \right] \quad (4)$$

where E is a constant and α is the extension ratio. In this case E is approximately three times the theoretical value for G in the equation of Guth and James. Bartenev also shows that for small stresses, if terms other than the first order are neglected, the equation of Guth and James approximates Equation 4 in which E then becomes:

$$E = 3 U k T \quad (5)$$

In order to make this work as complete as possible, the application of Bartenev's equation was considered to some extent, although most of the work was done before this equation came to our notice. As might have been expected, the empirical modifications required and results obtained appear to be closely similar.

The theoretical stress-strain relations presented here agree reasonably well with experimental data for low and moderate extensions of rubber containing

no reinforcing fillers. The simple theory represented by Equation 1 cannot be expected to hold for higher extensions, since it is based on a Gaussian formula for the distribution of displacement lengths, and this becomes increasingly inapplicable as the molecular extension exceeds more than about one third of the maximum extensibility. Various workers have expanded the theory for higher extensions by treatments involving inverse Langevin functions. Some degree of success has attended these efforts, but they are somewhat complex and inconvenient to apply. Partly for this reason, and partly because it seemed necessary to rely on a semiempirical equation for reinforced, as distinct from pure rubber, it was decided that an empirical modification of the simple equation should be sought in order to represent extensions up to 500 per cent.

Any empirical equation for unreinforced rubber must approximate Equation 1 for moderate extensions. A quite successful equation has been derived having the form:

$$F = G\gamma f(\alpha) \left[1 - \frac{1}{\alpha^3} \right] \quad (6)$$

in which γ is an arbitrary constant such that $\gamma f(\alpha) \simeq \alpha$ for moderate extensions. In this equation $f(\alpha)$ takes the form:

$$f(\alpha) = e^{p(\alpha-1)} \quad (7)$$

where p is a constant and equal to 0.31. By expanding $f(\alpha)$ the theoretical and empirical equations coincide exactly when $p\alpha - 1 = 0$ provided γ is chosen so that $\gamma f(\alpha) = \alpha$. The required expansion is:

$$f(\alpha) = e^{1-p} e^{p\alpha-1} = e^{1-p} \left[p\alpha + \frac{(p\alpha-1)^2}{2} + \frac{(p\alpha-1)^3}{3} + \dots \right] \quad (8)$$

Accordingly, in order to satisfy the condition $\gamma f(\alpha) \simeq \alpha$:

$$\gamma = \frac{1}{p} e^{p-1} = 1.618$$

The theoretical and empirical equations coincide exactly when $p\alpha - 1 = 0$, i.e., $\alpha = 3.23$ which represents 223 per cent extension. The equations may also be regarded as roughly equivalent at other extensions provided that powers of $(p\alpha - 1)$ may be neglected without errors considered serious in rubber tests. At 350 per cent extension the discrepancy is about 5 per cent; at 300 per cent about 2½ per cent; at 200 per cent, about 0 per cent; at 100 per cent, about 10 per cent; at 50 per cent, about 25 per cent; and at 0 per cent, about 65 per cent. This shows that the theoretical and empirical equations may be regarded as roughly equivalent for moderate extensions between 100 and 350 per cent. From the limited data obtained to date and even for moderate extensions, such differences as do exist lead to a better representation of the data by the empirical than by the theoretical equation. However, the greatest differences occur for extensions between 0 and 100 per cent; measurements for extensions less than 50 per cent have not been made and those for 50 and 100 per cent are not very accurate.

An equally successful semiempirical relation has been derived from consideration of Bartenev's equation. According to Bartenev's theory the empirical relation must approximate Equation 4 for low and moderate extensions:

$$F = G'\gamma f(\alpha) \left[\frac{1}{\alpha} - \frac{1}{\alpha^2} \right] \quad (9)$$

in which $\gamma f(\alpha) \approx 3\alpha$ for moderate extensions. The factor, 3, appears because the elastic constant, E , in Bartenev's equation is approximately three times the elastic constant, G , in the equation of Guth and James, and it is convenient to use the symbols G and G' throughout and define them as moduli, the prime indicating calculation from Equation 9. Here as before $f(\alpha)$ takes the form of Equation 7, but the constant p is now equal to $\frac{1}{2}$. The analysis of this function is the same as that given previously except for the inclusion of the factor in γ . Here γ takes the value 3.64. This analysis shows that for the lower extensions the theoretical and empirical equations agree more closely: At 200 per cent extension the discrepancy is about 10 per cent; at 150 per cent, about 3 per cent; at 100 per cent, 0 per cent; at 50 per cent, about 5 per cent; at 40 per cent, about 9 per cent, and at zero extension, about 20 per cent. The theoretical and empirical equations may be regarded as roughly equivalent for low and moderate extensions between 40 and 200 per cent.

These equations as they stand may be applied only to unreinforced rubber, which is substantially free from softening during extension. They are particularly accurate for high sulfur unaccelerated stocks. Accelerated stocks soften slightly during the first extension, but they are substantially unaffected by subsequent extensions that are less than the initial extensions, and it is customary to apply Equation 1 to rubber which has been conditioned by stretching. Reinforced rubber softens very much during the first extension, but during subsequent extensions the softening is reduced and becomes progressively less, provided the ultimate stress in the first extension is not exceeded. To obtain an empirical relation between stress and elongation for reinforced rubber, it is necessary to make measurements under conditions such that the degree of softening is relatively small. In the experiments to be described later, the stress-strain curves were considered after the third prestress.

Mullins¹ has shown that reinforced rubber behaves similarly to pure rubber at low extensions, following large prestresses. This experimental fact is recognized, and the data are successfully represented by introducing a new term into the extension function $f(\alpha)$ in the semiempirical Equations 6 and 9:

$$f(\alpha) = \exp. [p(\alpha - 1) + \mu(\alpha - 1)^4] \quad (10)$$

where the values of p are 0.31 and 0.5 for Equations 6 and 9, respectively. In this equation the new term $\mu(\alpha - 1)^4$ takes into account the very rapid increase in stress which occurs as the extension approaches the previous extension. This sharp upward swing of the stress-strain curve is shown in Figures 7 and 8; $\mu(\alpha - 1)^4$ becomes progressively less important as the elongation is reduced and as μ is reduced by lowering the concentration of reinforcing filler or by pre-stressing the rubber.

APPLICATION OF EQUATIONS TO UNREINFORCED RUBBER

The complete equation based on consideration of the theoretical relation of Guth and James comprises Equations 6 and 10:

$$F = G\gamma \left[1 - \frac{1}{\alpha^3} \right] \exp. [0.31(\alpha - 1) + \mu(\alpha - 1)^4] \quad (11)$$

The success of this empirical equation in representing stress-strain data for unreinforced rubber is shown in Figures 1 and 2 for extensions between 50 and 500 per cent and for accelerated and unaccelerated vulcanizates, respectively.

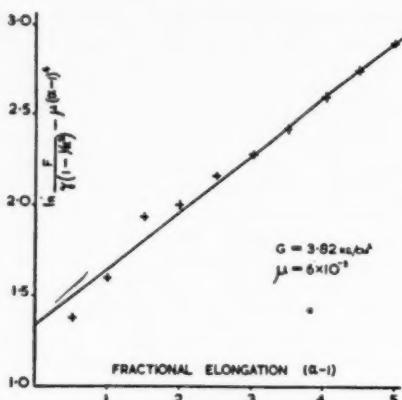


FIG. 1.—Application of Equation 11 to unreinforced rubber vulcanized with accelerator.

The data were obtained for the second extension in order to minimize the slight softening that occurs during extension. The slope of the lines is $p = 0.31$ and the intercept on the vertical axis is the logarithm of the modulus, G ; γ does not affect the slope of the graphs and, as explained previously, it was chosen to be 1.62 in order to make the moduli derived from the theoretical and empirical equations coincide approximately. For the unaccelerated vulcanizate (90 parts rubber and 10 parts sulfur) the empirical equation represents the data satisfactorily for extensions up to 500 per cent. The data for the accelerated stock (rubber 100, sulfur 3, mercaptobenzothiazole (MBT) 0.7, stearic acid 3.0, zinc oxide 5.0) suggest that the lowest extensions of 60 and 100 per cent do not fit so well, but in view of the inaccuracies in determining the stress at low extensions it is doubtful whether this departure has any significance. The modulus values obtained, $G = 3.8$ kg. per square cm. and $G = 4.2$ kg. per sq. cm.,

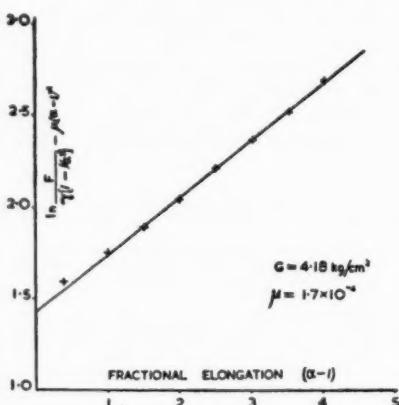


FIG. 2.—Application of Equation 11 to unreinforced rubber vulcanized without accelerator.

are of course substantially identical with the estimates generally obtained by application of Equation 1 to unreinforced rubber.

The alternative relation, based on considerations of Bartenev's equation, comprises Equations 9 and 10:

$$F = G'\gamma \left[\frac{1}{\alpha} - \frac{1}{\alpha^2} \right] \exp. [0.5(\alpha - 1) + \mu(\alpha - 1)^4] \quad (12)$$

where $\gamma = 3.64$. The success of this equation in representing the data is shown in Figure 3 for extensions between 50 and 500 per cent of the unacceler-

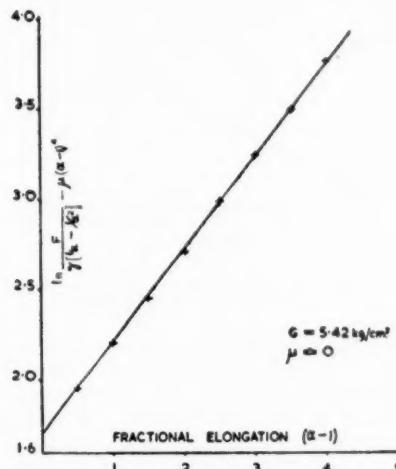


FIG. 3.—Application of Equation 12 to unreinforced rubber vulcanized without accelerator.

ated vulcanizate. The slope of the line is $p = \frac{1}{2}$, and the modulus value is higher than obtained by applying Equation 11.

APPLICATION OF EQUATIONS TO REINFORCED RUBBER

General experimental procedure.—Ring-shaped test-pieces were used and the experiments were carried out on a Goodbrand tensile testing machine, which is electrically-driven and makes an automatic recording of stress-strain curves. The rate of extension was 20 cm. per minute, and the tests were carried out in a controlled atmosphere at 70° F ($\pm 2^\circ$) and 65 per cent humidity. In these experiments twelve different prestresses were used—namely, 30, 40, 50, 60, 70, 80, 100, 120, 140, 160, 180, and 200 kg. per sq. cm.; there were two test-pieces for each prestress, the prestress being worked out on the original cross section. According to Mullins¹² much of the set is incomplete elastic recovery and disappears on heating; therefore, since only a small part of the observed set represents a true change in dimensions, it was not taken into account. There is a small genuine change, but it has only a small effect on the results.

In these experiments four successive stress-strain curves were drawn on the machine, the ultimate stress in each case being equal to the ultimate stress during the first extension, *i.e.*, the first prestress. The specimens were held at

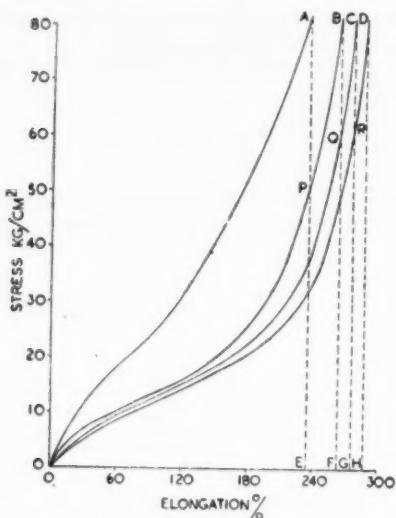


FIG. 4.—Stress-strain curves of carbon-reinforced rubber after successive prestress of equal magnitude.

the prestress for 30 seconds, and then the stress was released. In each case approximately 1 minute elapsed between successive extensions although this time was not precisely controlled.

A typical set of curves is shown in Figure 4. Most of the softening takes place during the first extension, and little occurs during the fourth extension. *P, Q, R* are the points corresponding to the ultimate extension reached on the previous curve. The difference between the areas *OAE* and *OPE* is proportional to the difference in energies required to extend the rubber successively to the same elongation, and this difference has been taken to be approximately proportional to the energy absorbed in the rubber during the first extension because of rupture of bonds. Similarly the energy absorbed during the second and third extensions has been taken to be proportional to the difference in the areas *ORF* and *OQF*. The areas were measured with a planimeter and converted to energies in calories per cc. The energy absorbed during the third extension is small relative to the energy absorbed during the first extension, as would be expected from the much smaller degree of softening during the third extension. The energy absorbed and the softening during the fourth extension would be smaller still, and as a necessary approximation it has been neglected in this work, although this must undoubtedly lead to some inaccuracy.

Tread Vulcanizate Containing MPC Black. A study was made of a compound mixed according to the formula:

	Parts by weight
Rubber	100.0
MPC black	50.0
Stearic acid	2.0
Zinc oxide	5.0
Santocure	0.8
Sulfur	2.5
Antioxidant	1.0

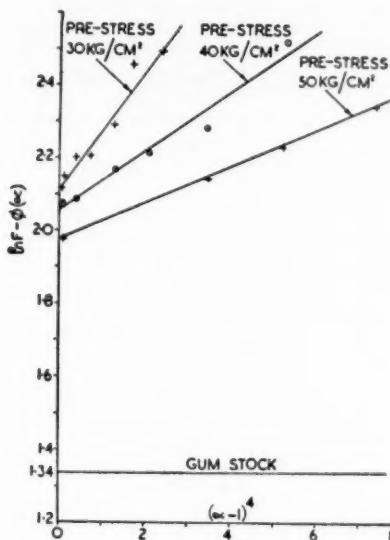


FIG. 5.—Application of Equation 11 to rubber reinforced with carbon black.

and cured 55 minutes at 281° F. Equation 11 derived from Guth and James may be written:

$$\ln F - \Phi(\alpha) = \ln G + \mu(\alpha - 1)^4 \quad (13)$$

where

$$\Phi(\alpha) = 0.31(\alpha - 1) + \ln 1.62 \left[1 - \frac{1}{\alpha^3} \right] \quad (14)$$

Hence if the semiempirical equation represents the data satisfactorily, a plot of $\ln F - \Phi(\alpha)$ against $(\alpha - 1)^4$ should give a straight line with slope μ and intercept $\ln G$. Typical curves are given in Figures 5 and 6 which show how

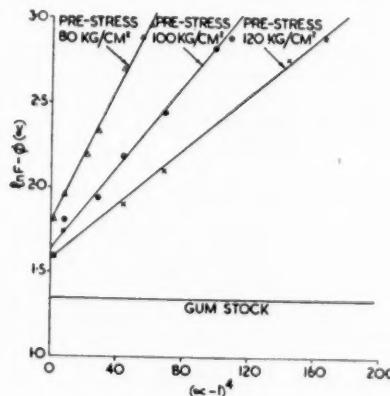


FIG. 6.—Application of Equation 11 to rubber reinforced with carbon black.

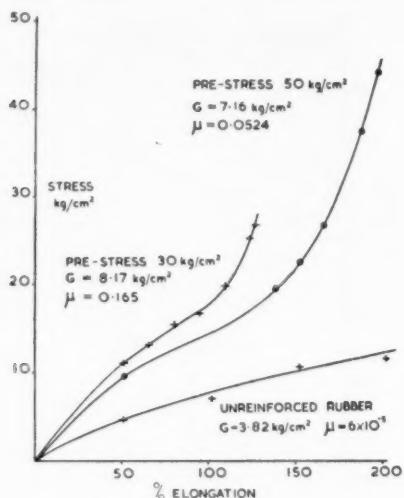


FIG. 7.—Influence of carbon black on stress-strain curves and effect of prestress.

prestressing reduces G and the slope or extension factor, μ . Equally satisfactory graphs have been obtained for all prestresses in the range 30 to 200 kg. per sq. cm., and for the other compounds considered in this paper. The effect of carbon black loading will not be considered here, but the equation has been satisfactorily applied for MPC black loadings from 10 to 60 parts by weight. In some instances, however, a slight tendency to upward curvature of the graphs

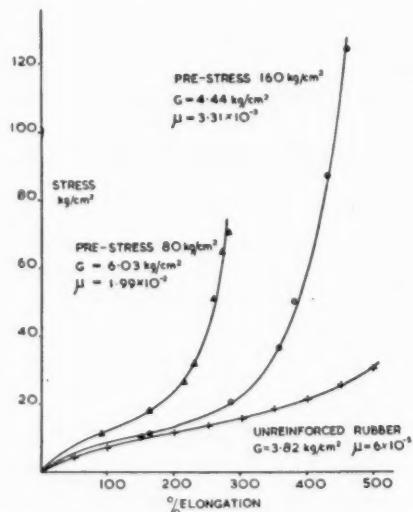


FIG. 8.—Influence of carbon black on stress-strain curves and effect of prestress.

was noted for prestresses between 160 and 200 kg. per sq. cm.; this suggests that for high prestresses and high extensions the equation does not fit the data quite so well.

The stress-strain curves for prestressed reinforced rubber are illustrated in Figures 7 and 8, the experimental points being represented by the crosses. These graphs show that the extension at which the curve begins to swing upwards increases with prestress and that this behavior is represented by changes in μ .

Equation 12 has been applied to a tread vulcanizate containing an HAF black, and it was equally successful in representing the experimental data. The values for G' obtained by using this equation are higher than the values of G from Equation 11, but are directly proportional to them. The two moduli are compared in Figure 9, in which the lowest experimental point represents the unreinforced rubber consisting of rubber and sulfur only.

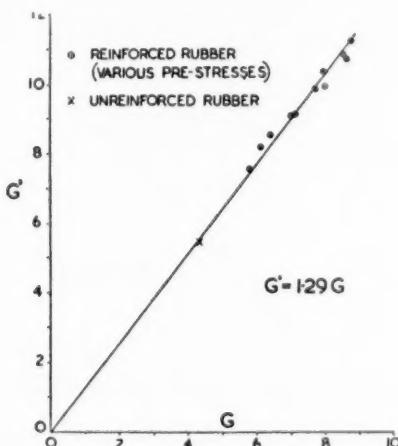


FIG. 9.—Relation between moduli, G and G' , obtained from Equations 11 and 12, respectively.

These results indicate that, for the range of extensions used in these experiments, it is immaterial which of the equations is used, except in so far as the one may be slightly more accurate than the other or more sound in its theoretical basis. Values of μ obtained from the two equations are almost identical as shown in Figure 10.

INTERPRETATION OF G AND μ

The explanation of the elasticity of rubberlike polymers in terms of chemical cross-linkages between the rubber macromolecules and the thermal energy of the system is now well established. In regard to reinforced rubber, it is convenient and instructive to draw a crude analogy with a chemically cross-linked polymer and to attempt a rough form of interpretation in terms of linkages between rubber molecules. These linkages between the rubber molecules are presumed to occur through carbon particles as a result of adsorptive or chemisorptive attachments between the carbon and the rubber. This concept is

illustrated in Figure 11 in which linkages are formed by the particles *B* and *C* but not by *A*.

For moderate extensions of unreinforced rubber, the theoretical and empirical equations for the stress-strain curve for approximately equivalent, and so G can be taken to be proportional to the number of cross-links in accordance with the Equation 2. In this case, μ in the extension function (Equation 10) is very small, so the term $\mu(\alpha - 1)^4$ can be neglected. In reinforced rubber this is true only when a small amount of reinforcing material is present or when μ has been drastically reduced by applying a large prestress. The extension factor, μ , may therefore be taken to represent roughly the deviation from the theoretical equation for a given extension. This departure from theoretical behavior decreases very rapidly as the extension is reduced. Hence, G in the semiempirical equation may be said to determine stiffness at the lower extensions; it has been regarded as representing roughly a theoretical component of the stiffness with deviation from theoretical behavior represented by μ .

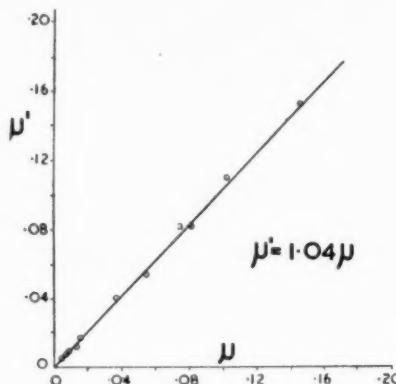


FIG. 10.—Relation between extension factors, μ and μ' , obtained from Equations 11 and 12, respectively.

The effect of incorporating a mass of bonded carbon particles in rubber instead of a simple chemical cross-linking agent is not easy to predict. Cross-linking by carbon particles means that the linkages take place through carbon particles instead of through links which approximate mathematical points, and there is also the general effect of a mass of carbon particles in the rubber to be considered. However, in view of the presence of carbon particles at the junction points in reinforced rubber it is interesting to note that James and Guth⁴ have shown that the forces developed by a cross-linked network are theoretically the same whether the junction points are treated as free or fixed at their most probable positions. As a rough working hypothesis, it seems reasonable to assume that G is roughly proportional to the number of cross-links of all kinds (including sulfur linkages) present in unit volume. Making this assumption:

$$G \doteq \Psi U \quad (15)$$

where the constant of proportionality $\Psi = \beta kT$ (cf. Equation 2). The constant, β , may depend to some extent on the quantity of carbon black in the

rubber and on the number of linkages which it forms. It is probable that some error will arise in using Equation 15, owing to changes in β , and therefore Ψ , because of alterations in the distribution of chain displacement lengths as the degree of cross-linking is altered by prestressing the rubber. In view of all these considerations, Equation 15 is proposed only as an approximate relation which has been found useful in considering the softening of rubber by applied stress.

The experimental results may be generally expressed by saying that, at low extensions, the stiffness of reinforced rubber is determined mainly by G , and its behavior is similar to the theoretical behavior of an ordinary cross-linked polymer, whereas at high extensions the stiffness is mainly determined by μ and its behavior is entirely different from that predicted by the simple theory. For unreinforced rubber the departure from simple theory represented by the sharp upward swing in the stress-strain curve is generally attributed to the effect of the limited extensibility of the network. For reinforced rubber (Figures 7 and 8) the upward swing occurs earlier at elongations determined by the value of μ , which depends on the stress the rubber has experienced and the

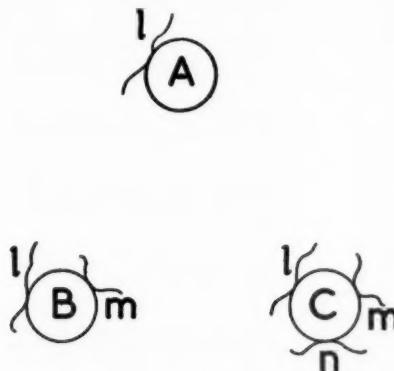


FIG. 11.—Formation of linkages between rubber molecules through carbon particles.

quantity of carbon black it contains. A reasonable explanation of these results is that the linkages formed by the carbon particles in effect limit the maximum extensibility of the network and that continued extension is possible only because more bonds are ruptured when the prestress is exceeded. One of the most striking characteristics of reinforcement by carbon black appears to be the relatively large values of μ which result, and this is presumably because the cross-linking is by means of particles consisting of more than a few atoms.

ANALYSIS OF SOFTENING BY APPLIED STRESS

Table I shows a typical set of data for a tread compound containing 50 parts of MPC black and cured 55 minutes at 281° F.

Figure 12 shows how G varies with the quantity of energy, H , absorbed in the rubber because of various prestresses. If G is a rough measure of the number of cross-linkages, the inverse slope of the curve $\frac{dH}{dG} \left(\simeq \frac{1}{\Psi} \frac{dH}{dU} \right)$ from Equation 15

TABLE I
STRESS-STRAIN DATA FOLLOWING THIRD PRESTRESS
(Tread compound containing 50 parts MPC black; cure, 55 minutes at 281° F.)

Total energy	Elong. absorbed	Prestress at third in three prestress prestresses (kg./sq. in.)	Elong. (%, sec.)	F_a (kg./sq. cm.)	Elong. (%, sec.)	F (kg./sq. cm.)						
30	127	0.16	50	11.7	64	13.0	71	14.3	86	15.9	93	17.3
40	168	0.32	50	10.6	71	12.7	86	14.2	107	16.6	129	20.2
50	193	0.49	50	10.0	71	12.3	107	15.8	129	18.3	143	20.5
60	225	0.83	50	9.5	71	11.5	107	15.0	143	18.8	171	23.0
70	254	1.01	71	10.8	107	14.0	143	17.0	179	21.3	200	27.3
80	270	1.32	71	11.0	107	14.0	143	17.0	179	20.8	229	33.0
100	325	2.18	107	12.3	143	15.0	179	18.0	214	21.5	250	28.3
120	372	3.01	143	13.5	179	16.5	214	19.0	250	23.0	286	31.5
140	397	3.65	143	14.5	179	17.5	214	20.0	286	29.0	336	34.0
160	434	5.19	179	16.0	214	19.0	250	22.0	286	25.0	357	48.5
180	497	6.74	179	13.5	250	18.5	286	20.5	357	30.0	393	43.5
200	533	18.7	214	17.0	250	19.5	321	24.0	393	35.5	429	49.5

^a F = force per unit area of original cross-section.

gives an indication of the energy due to rupture of a single linkage. After low prestresses, G , and hence the number of linkages, is high, but $\frac{dH}{dG}$ is small indicating that only weak linkages are broken. After high prestresses G is small, not much greater than for unreinforced rubber, whereas $\frac{dH}{dG}$ is large, suggesting that strong linkages are now being broken. Thus only a relatively small number of strong linkages are introduced by reinforcement. Although the quantity $\frac{dH}{dG}$ may be legitimately used in forming the broad picture of the nature of the linkages in reinforced rubber, it cannot be used with much confidence as a general measure of linkage strength because of theoretical complications arising out of the distinction between bonds and linkages. This can be understood by reference to Figure 11 in which particle B has two attachments (bonds) and

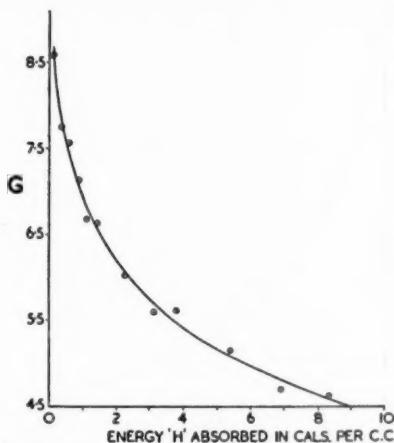


FIG. 12.—Relation between modulus and energy irreversibly absorbed in rubber during three successive prestresses.

forms one linkage between molecules l and m , whereas particle C has three attachments and forms linkages between l and m , l and n , and m and n . Thus for any one carbon particle two bonds form one linkage, three bonds form three linkages, and n bonds form $\frac{1}{2}n(n - 1)$ linkages so that the energy required to rupture one bond may in some instances destroy more than one linkage; $\frac{dH}{dG}$ will then be a measure of the energy to rupture a linkage, not a bond.

Another possible measure of the strength of a linkage would be the force per link required to rupture that linkage. It is to be expected that the force per linkage depends on the stress applied to the rubber and on the number of linkages, U , per unit volume. The dimensions of stress are (M) , (L^{-1}) , and (T^{-1}) , and the dimensions of U are (L^{-3}) . An expression for the force per linkage in terms of these quantities must have the dimensions of force, *i.e.*, (M) , (L) , and (T^{-2}) . Therefore, since the force per linkage will be directly proportional to

the prestress, S :

$$\frac{(M)(L^{-1})(T^{-2})}{(L^{-3})} = (M)(L)(T^{-2})$$

This condition is satisfied provided that $\rho = \frac{2}{3}$. It is, therefore, probable that the force per linkage may be satisfactorily expressed in terms of the quotient $\frac{S}{U^{\frac{1}{2}}}$. The ultimate justification of any measure of linkage strength lies in experiment, and a valid measure of this property must be such that the proportion of linkages introduced by the filler with strengths between various limits is independent of the loading of filler. In other words, although the quantity of reinforcing filler in the rubber determines the number of linkages, it cannot alter the true strength distribution of those linkages. In practice it was found that

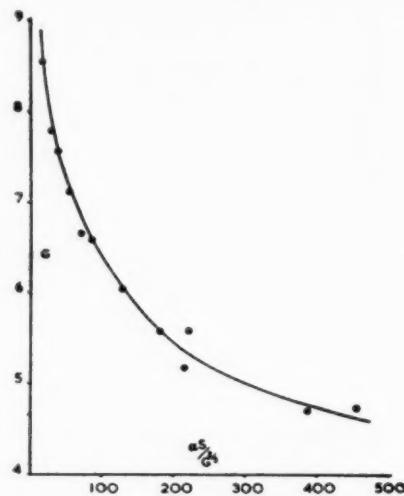


FIG. 13.—Relation between modulus and stress concentration per linkage applied to rubber.

a satisfactory measure of linkage strength in this respect could be obtained by multiplying $\frac{S}{U^{\frac{1}{2}}}$ by the extension ratio, α , corresponding to S . Preliminary experiments not recorded in this paper indicated that the value of $\frac{\alpha S}{U^{\frac{1}{2}}}$ required to break a linkage is a valid measure of linkage strength, notwithstanding the enormous variation of α with the content of reinforcing filler. Since α is dimensionless, this product still has the dimensions of a force and may still be taken to be a measure of the force per linkage. If U is taken to be roughly proportional to G in accordance with Equation 15, the quantity $\frac{\alpha S}{G^{\frac{1}{2}}}$ is therefore a measure, though not an absolute one, of the force per linkage and should determine the degree of softening following the application of stress. In

Figure 13 G is plotted against $\frac{\alpha S}{G^4}$. The comparatively large changes in G when the force per linkage is small signify breakage of a relative large number of weak linkages. The small changes in G when $\frac{\alpha S}{G^4}$ is large show that a relatively small number of strong linkages are broken by the highest prestresses. The small difference in these conditions between the G values for reinforced rubber and for gum stocks shows that only a small number of strong carbon-rubber linkages remain unbroken after the highest prestress (200 kg. per square cm.).

We may define a linkage strength factor, X , as the value of $\frac{\alpha S}{G^4}$ required to break the linkage. If $G = \Psi U$, $dU = \frac{dG}{\Psi}$, so that changes in the number of links per unit volume are expressed in terms of Ψ . In practice Ψ has been dropped and G has been used as a measure, though not an absolute one, of the

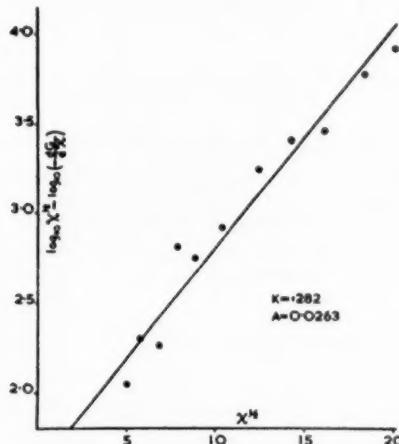


FIG. 14.—Graph of function expressing distribution of linkage strengths (X) for MPC black.

linkage concentration. The experimental prestresses are in the range 30 to 200 kg. per sq. cm., and data on the weakest linkages which rupture between 0 and 30 kg. per sq. cm. are not available.

In the range of easily breakable linkage strengths covered by these experiments, the distribution has been satisfactorily represented by the function:

$$dG = -AX^4e^{-KX^4}dX \quad (16)$$

where dG is proportional to the number of linkages with breaking strengths between X and $X + dX$. This distribution function was obtained empirically from the tangents $\frac{dG}{dX}$ for different X values in Figure 13.

In Figure 14 $\log_{10}X^{\frac{1}{3}} - \log_{10}\left[\frac{-dG}{dX}\right]$ is plotted against $X^{\frac{1}{3}}$, the slope of the line being $K \log_{10} e$. Although the experimental points on this graph suggest the relation may not be linear, this is not borne out by other data and is believed to be due to experimental errors.

If G^* represents the modulus due to strong linkages (including sulfur linkages), which cannot be ruptured by stress concentration of the magnitude used in these experiments, then:

$$G = G^* + G_r F(X) \quad (17)$$

where G_r is a constant proportional to the total number of linkages which can readily be broken by prestressing. $F(X)$, which is based on the distribution function in Equation 16, is a function of the strength, X , of the weakest unbroken linkages present; it is zero when only the unbreakable linkages are left and unity when no linkages have been broken.

If the distribution function (Equation 16) is integrated over the range of X from zero to infinity:

$$\int_0^\infty X^{\frac{1}{3}} e^{-KX^{\frac{1}{3}}} dX = \frac{2}{K^{\frac{2}{3}}} \quad (3) = \frac{4}{K^3} \quad (18)$$

so that

$$F(X) = \frac{K^3}{4} \int_X^\infty X^{\frac{1}{3}} e^{-KX^{\frac{1}{3}}} dX, \quad G_r = \frac{4A}{K^3} \quad (19)$$

The application of G^* and G_r will be discussed later.

TABLE II
VALUES OF G AND μ

G	μ
3.71 reinforced rubber	2.4×10^{-3}
4.06	2.5×10^{-3}
4.09	3.1×10^{-3}
3.82	1.8×10^{-3}
3.82 unreinforced rubber	6×10^{-5}

The variation of μ with $\frac{\alpha S}{G^{\frac{1}{3}}}$ is shown in Figure 17. Whereas the lowest value of G (Figure 13) is close to the value of G for unreinforced rubber, the corresponding value of μ in Figure 17 is still much greater than for unreinforced rubber. In Table II, a comparison is made between values of G and μ obtained in some other experiments after applying a large prestress. For moduli which are substantially equivalent the extension factor of rubber which has been cross-linked by carbon black particles is much higher than the extension factor of rubber which contains only the chemical cross-links due to vulcanization. A high extension factor relative to modulus is, therefore, characteristic of cross-linking by carbon particles. This is presumably because the cross-linkages are formed through relatively large rigid carbon particles or chains of carbon particles as a result of adsorption or chemisorption.

EFFECT OF HEAT TREATMENT

The data of Table I record part of an experiment in which the effect of heat treatment of a rubber-channel black stock was investigated. The rubber and

TABLE III
EFFECT OF HEAT TREATMENT (MPC) BLACK

Prestress (kg./sq. cm.)	Extension (%)	Stress (kg./sq. cm.)	
		Normal	Heat-treated
30	50	11.7	10.3
	71	14.3	12.9
	93	17.3	15.5
	114	22.4	19.1
60	50	9.5	10.3
	107	15.0	16.3
	171	23.0	27.8
	200	33.3	44.8
100	107	12.3	14.0
	179	18.0	20.8
	214	21.5	27.3
	286	46.0	78.0
140	143	14.5	16.5
	214	20.0	23.0
	286	29.0	47.0
	357	73.0	137.5
180	179	13.5	16.5
	286	20.5	28.0
	357	30.0	66.5
	429	68.0	167.0

black were mixed together and the stock was divided into two parts, one of which was allowed to stand overnight before the mix was completed; the other half was heated for 45 minutes at 316° F in a steam pan before completion the next day. Some of the experimental data are compared in Table III. These

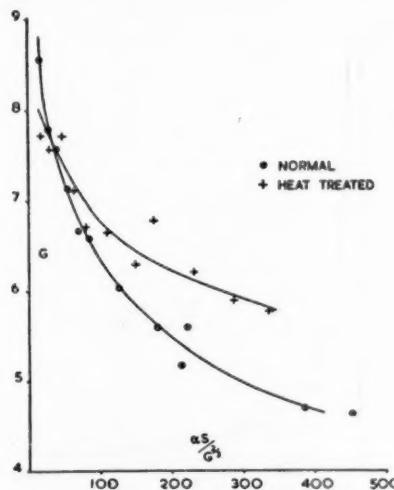


FIG. 15.—Relation between modulus and stress concentration per linkage for normal and heat-treated rubbers containing MPC black.

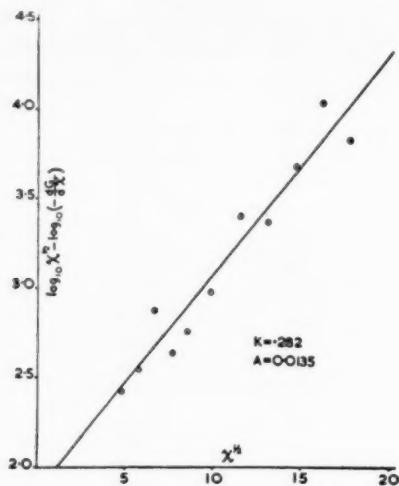


FIG. 16.—Graph of function expressing distribution of linkage strengths (X) for heat-treated rubber containing MPC black.

results show that, for large extensions after high prestresses, the difference due to heat treatment was large, but for small extensions following low prestresses little effect was observed. A similar story is told by data from the initial stress-strain curves. For instance at 40 kg. per sq. cm. the extension of both rubbers was 168 per cent, whereas at 200 kg. per sq. cm. the heat-treated rubber extended 438 per cent, compared with 533 per cent for the normally treated rubber. This is striking proof of the inadequacy of the conventional methods

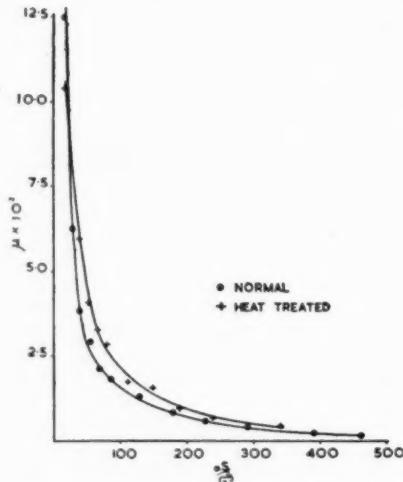


FIG. 17.—Dependence of extension factor on stress concentration per linkage applied to rubber.

TABLE IV
EFFECT OF HEAT TREATMENT (MPC BLACK)

<i>G</i>	μ	
	Normal	Heat-treated
6.0	0.010	0.007
6.5	0.017	0.016
7.0	0.027	0.029
7.5	0.044	0.054

of expressing the stress-strain properties of reinforced rubber in terms of the extension at an arbitrary stress or the stress at some arbitrary extension.

Equation 11 has been successfully applied to heat-treated rubber. In Figure 15 *G* is plotted against $\frac{\alpha S}{G^4}$ for both the heat-treated and the normal rubbers. The diagram shows that, after small prestresses, there are fewer cross-linkages in the heat-treated stock, but that the treatment is responsible for a remarkable increase in the number of strong linkages which survive the highest stresses applied to the rubber in these experiments. In Figure 16 the slope of the line is equal to that for the untreated rubber so that *K* = 0.282 as before, but *A* has been reduced to about one-half its previous value and *G_r*, the component of the modulus due to easily breakable linkages, has been reduced by half, whereas the component *G^{*}*, due to strong linkages, has been increased.

The effect of heat treatment on the extension factor following various prestresses is shown in Figure 17, which is similar to the figure in which *G* is plotted against $\frac{\alpha S}{G^4}$. Table IV shows the extension factors corresponding to various values of *G* for normal and for heat-treated rubber.

TABLE V
EFFECT OF HEAT TREATMENT (HAF BLACK)

Prestress (kg./sq. cm.)	Extension (%)	Stress (kg./sq. cm.)	
		Normal	Heat-treated
30	50	12.1	10.4
	71	15.1	13.1
	93	19.3	16.0
	114	28.0	21.2
60	50	10.5	11.0
	107	17.8	17.8
	143	25.5	25.5
	186	54.0	55.0
100	71	11.5	12.0
	143	18.0	19.8
	229	42.0	54.0
	250	61.5	82.0
140	143	17.0	17.0
	214	25.5	26.0
	286	58.0	66.0
	321	98.2	115.0
180	179	18.5	17.5
	286	33.0	34.0
	357	83.0	95.5
	407	156.5	174.0

The influence of heat treatment on G and μ for a high abrasion furnace black stock is much less striking than it is in a rubber-channel black stock. Part of the experimental data is shown in Table V.

Table VI gives a comparison of G and μ obtained after various prestresses for the normal and heat-treated stocks. There is considerable irregularity in

TABLE VI
EFFECT OF HEAT TREATMENT (HAF BLACK)

Prestress (kg./sq. cm.)	Modulus, G		Extension factor, μ	
	Normal	Heat-treated	Normal	Heat-treated
30	8.73	7.81	2.53×10^{-1}	1.50×10^{-1}
40	8.50	7.63	1.48×10^{-1}	1.11×10^{-1}
50	8.52	8.52	1.04×10^{-1}	9.95×10^{-2}
60	7.97	8.17	7.54×10^{-2}	7.33×10^{-2}
70	7.94	7.88	5.45×10^{-2}	5.57×10^{-2}
80	7.70	8.00	3.75×10^{-2}	4.20×10^{-2}
100	8.02	7.52	2.30×10^{-2}	2.80×10^{-2}
120	6.68	7.69	1.52×10^{-2}	1.96×10^{-2}
140	6.98	6.68	1.34×10^{-2}	1.37×10^{-2}
160	6.36	6.22	7.51×10^{-3}	1.00×10^{-2}
180	6.11	5.93	5.81×10^{-3}	6.45×10^{-3}

the values of G for the lower prestresses on the heat-treated rubber. Equation 11 used to obtain G and μ fitted the data satisfactorily; hence, the irregularities presumably result from differences between the samples used for the various prestresses. The cause of these differences is not known. The extension factor of the heat-treated stocks appears to be slightly less than normal after low prestresses and greater than normal after high prestresses. Considering the irregularity in the values of G there does not appear to be any appreciable change in G due to heat treatment for either small or large prestresses.

COMPARISON BETWEEN REINFORCING FILLERS

The differences in properties between channel black and high abrasion furnace black are of particular interest in any study of reinforcement and accordingly a comparison between these blacks was made using the methods described previously; the compounds were mixed to the following formula and cured 55 minutes at 281° F:

	Parts by weight
Rubber	100.0
MPC black	50.0
HAF black	—
Stearic acid	2.0
Zinc oxide	5.0
Santocure	0.8
Sulfur	2.5
Antioxidant	1.0

Part of the experimental data is recorded in Table VII. For large extensions following high prestresses the stiffness imparted by HAF black greatly exceeds the stiffness due to channel black but for low extensions after low prestresses little difference is observed. The differences observed are even greater than those between normal and heat-treated stocks.

Equation 11 has been successfully applied to rubber reinforced with HAF

TABLE VII
COMPARISON BETWEEN MPC AND HAF BLACKS

Prestress (kg./sq. cm.)	Extension (%)	Stress (kg./sq. cm.)	
		MPC black vulcanizate	HAF black vulcanizate
30	50	11.3	12.1
	71	14.0	15.1
	93	17.7	19.3
	114	23.4	28.0
60	50	9.5	10.5
	107	15.5	17.8
	143	19.3	25.5
	186	29.5	54.0
100	107	13.3	14.8
	143	15.8	18.0
	200	—	28.3
	250	30.5	61.5
140	143	14.0	17.0
	179	16.5	21.0
	214	20.0	25.5
	286	28.0	58.0
160	179	15.0	18.5
	250	20.5	—
	321	—	65.5
	357	43.5	107.0
180	179	13.0	18.5
	286	21.0	33.0
	357	30.5	83.0
	393	43.5	133.0

black. In Figure 18 G is plotted against $\frac{\alpha S}{G^{\frac{1}{2}}}$ for the rubbers containing both the HAF black and MPC black. The diagram shows that the rubber reinforced by HAF black has, according to the authors' interpretation, not only more linkages but a considerably greater number of strong linkages. Applying Equation 16, $K = 0.270$ for HAF black, a value substantially the same as that

TABLE VIII
VARIATIONS IN EXTENSION FACTOR

Prestress (kg./sq. cm.)	Extension factor (μ)	
	MPC black vulcanizate	HAF black vulcanizate
30	1.69×10^{-1}	2.53×10^{-1}
40	6.62×10^{-2}	1.48×10^{-1}
50	4.50×10^{-2}	1.04×10^{-1}
60	3.37×10^{-2}	7.54×10^{-2}
70	2.70×10^{-2}	5.45×10^{-2}
80	1.96×10^{-2}	3.75×10^{-2}
100	1.16×10^{-2}	2.30×10^{-2}
120	7.75×10^{-3}	1.52×10^{-2}
140	5.26×10^{-3}	1.34×10^{-2}
160	3.60×10^{-3}	7.51×10^{-3}
180	2.50×10^{-3}	5.81×10^{-3}
200	1.94×10^{-3}	3.98×10^{-3}

obtained previously for MPC black. The differences in extension factor are shown in Table VIII.

Only a brief account is possible here of comparisons between other reinforcing fillers, those which will be dealt with including fine thermal black (P-33), calcium silicate (Silene), and magnesium carbonate. With the exception of P-33, which had 36 parts by volume, the concentration of filler was 26 parts by volume, which corresponds to 50 parts by weight of carbon black.

The compounds were mixed according to the following formulas:

	Parts by weight		
Smoked sheet rubber	100.0	100.0	100.0
P-33	70.0	—	—
Silene	—	55.3	—
Magnesium carbonate	—	—	59.3
Stearic acid	2.0	2.0	2.0
Zinc oxide	5.0	5.0	5.0
Sulfur	2.5	2.5	2.5
Santocure	0.7	0.7	0.7
Antioxidant	1.0	1.0	1.0

Table IX shows some of the data which were obtained at a cure of 55 minutes at 281° F.

In each case Equation 11 was applied successfully, and in Figure 18 the curves for G plotted against $\frac{\alpha S}{G^2}$ are shown with the curves for channel black

TABLE IX
DATA FOR MISCELLANEOUS REINFORCING FILLERS

Prestress (kg./sq. cm.)	Extension (%)	Stress at extension (kg./sq. cm.)		
		Silene (26 parts by vol.)	Magnesium carbonate (26 parts by vol.)	P-33 (36 parts by vol.)
30	71	7.8	9.3	10.8
	107	—	12.1	13.8
	214	17.1	25.2	—
60	143	8.8	10.0	12.8
	286	15.0	18.5	23.8
	357	20.0	29.8	37.0
100	179	8.8	9.5	—
	429	19.0	24.8	29.0
	500	25.5	42.5	48.0
120	179	9.5	8.5	10.0
	321	15.0	14.5	—
	500	25.0	29.5	36.0
140	179	8.5	8.5	10.5
	429	18.0	20.0	23.5
	500	21.5	28.5	31.0

and HAF black. These curves are all for equal volume concentration equivalent to 50 parts by weight of black. The curve for the vulcanizate containing 70 parts by weight of P-33 is shown in Figure 19.

MECHANISM OF SOFTENING BY APPLIED STRESS

To account for the stiffness of reinforced rubber, it is necessary to postulate some kind of attachment of the reinforcing particles to the rubber molecules. Theoretical approaches to this problem by considering the stresses in rubber in the region of spherical particles have been made by Weiss¹³, Rehner¹⁴, Smallwood¹⁵, Guth¹⁶, and Guth and Gold¹⁷. By computing the hydrodynamic interaction of pairs of particles Guth and Gold added a term to Smallwood's equation, obtaining the expression:

$$E^* = E(1 + 2.5C + 14.1C^2) \quad (20)$$

where E^* is Young's modulus for the reinforced rubber, E is Young's modulus for the rubber matrix, and C is the volume concentration of filler. To account for the effect of the presence of chainlike groupings of carbon particles Guth has

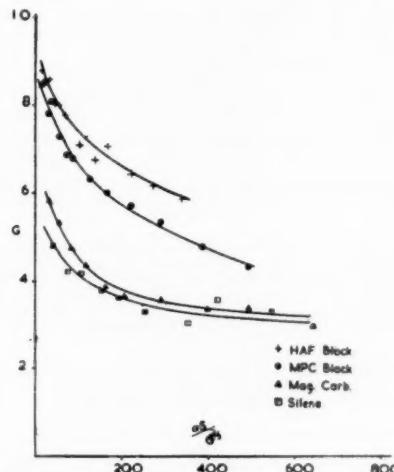


FIG. 18.—Relation between modulus and stress concentration per linkage for rubber containing 26 parts by volume of various fillers.

considered rodlike particles of fillers and obtains the equation:

$$E^* = E(1 + 0.67fC + 1.62f^2C^2) \quad (21)$$

where f is the shape factor of the rod.

Although these equations have been shown by Guth¹⁸ and by Cohan¹⁹ to conform to experimental data for certain fillers, they take no account of the softening of reinforced rubber by application of stress so that, as theories of stiffness, they are incomplete and can hardly be regarded as satisfactory in offering an explanation of the mechanism of reinforcement in which factors other than stiffness are important. However, it may perhaps be argued that the softening of reinforced rubber with stress can be accounted for by changes in f in Equation 21. This possibility arises in the interpretation in terms of cross-linkages through carbon particles put forward in the present paper. For a given number of attachments between rubber molecules and carbon particles,

there will be a higher proportion of linkages through the carbon if chain structure is present, and the number of linkages will be reduced by rupture of the carbon chains. This is shown in Figure 20, which represents three particles each having one attachment to the rubber. Individually the particles do not form a linkage, but if grouped into a coherent chain of particles they form three linkages between the molecules *l*, *m*, and *n*.

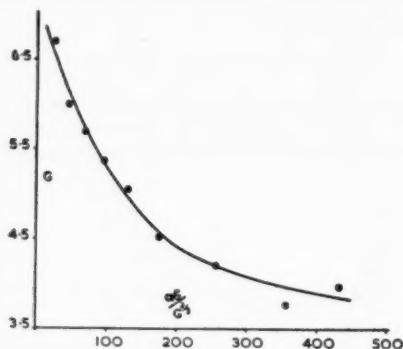


FIG. 19.—Relation between modulus and stress concentration per linkage for rubber containing 36 parts by volume of P-33 black.

Mullins¹ ascribed softening of reinforced rubber with stress to breakdown of bonds between filler particles and to filler-rubber bonds. He appears to have emphasized filler chain structure in this connection, particularly in a later publication²⁰, where there is little mention of bonds between filler and rubber.

The work of Ladd and Wiegand²¹ led them to conclude that chain structure, which is present in carbon black before incorporation into the rubber, largely

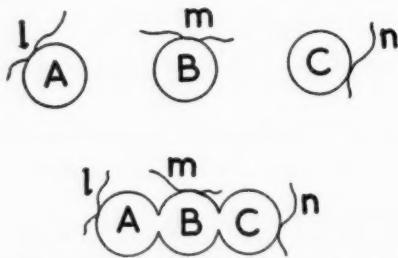


FIG. 20.—Effect of primary carbon chain structure on linkage formation.

persists after mixing and milling, a view which has received support from work by the present authors²² and by Cohan and Watson²³. It was concluded²² that, although there is a limited mobility of carbon particles in rubber, there is no evidence of extensive catenation of carbon particles within the rubber following milling. Remilling the rubber-black stock following heat treatment under certain conditions can break down the carbon chain structure permanently,

as is indicated by the enormous increase in electrical resistivity, which shows no appreciable change on further heating. The chains of carbon particles, characteristic of the black, which undoubtedly exist in rubber are interpreted as portions of original structures formed during manufacture of the black and which have survived the stresses during normal milling procedure.

The term "characteristic structure" was later adopted by the authors²⁴ to express this concept, but the term "primary structure" used by Cohan and Watson seems to be preferable. It seems unlikely that primary structures which have withstood the severe action of remilling will be broken by small or moderate extensions of the rubber vulcanizate. The term "fortuitous structure" was used²⁴ to describe chainlike groupings of particles formed by adjacent particles within the rubber, but here also the term "secondary structure" used by Cohan and Watson is better. In Hevea rubber, according to electrical resistivity measurements, this structure appears to be influenced by flexing, stretching, and heating, there being some increase in conductivity when the rubber is heated following flexing or stretching. Previous work²⁴, which involved comparisons of the changes in electrical resistivity and tensile stiffness accompanying prestressing, suggested that the softening of rubber with stress cannot be attributed to rupture of secondary chain structure, which appears to be relatively weak and presumably only makes a contribution to stiffness at very low extensions. In certain circumstances involving heating and stressing the rubber, the stiffness was even increasing while the electrical conductivity decreased sharply. Therefore the softening of rubber with stress is attributed mainly to rupture of carbon-rubber bonds.

The research reported here has provided fresh evidence that the changes in stiffness of reinforced rubber under various experimental conditions cannot be interpreted in terms of chain structure or shape factor. For instance the profound changes in stiffness with applied stress are also obtained with fine thermal black P-33 (Figure 19), which has little chain structure and has in fact been used by Guth¹⁸ and Cohan²⁵ to test Equation 20, which is intended to apply to spherical particles having no shape factor. Moreover, the values of G for rubber containing Silene and magnesium carbonate are so low after moderate and low prestresses (Figure 18) that no appreciable stiffening of the rubber by these fillers can have survived. This means that, even if it could be maintained that these fillers have shape factors which can be reduced by stressing the rubber, it would still be necessary to assume that substantially all the filler-rubber bonds which form linkages have been broken. However, since Silene consists of approximately spherical particles of calcium silicate which do not appear to exhibit chain structure, it does not seem possible to explain any part of the softening of rubber containing this filler in terms of shape factor. The particles of magnesium carbonate on the other hand are asymmetric, and therefore possess a shape factor, but they do not appear to show chain structure. This makes it difficult to attribute softening to reduced shape factor, for it is inconceivable that the magnesium carbonate particles are broken by stressing the rubber matrix. Another fact to be noted is that softening by applied stress is also observed in rubber after heat treatment as described earlier. The resistivity of such rubber is very high (approximately 10^{12} ohm-cm. for rubber containing MPC black) and is practically unchanged by stressing, indicating that little primary or secondary structure remains. Moreover, the softening due to applied stress (Figure 18) is no greater for the HAF black than it is for the MPC black, although the HAF black has considerably more chain structure to break down.

Admittedly, as first shown by Bulgin²⁶, there is plenty of evidence that the resistivity of Hevea rubber containing channel or furnace black is increased by momentarily extending the rubber and this implies that the secondary structure has been disturbed and reduced in amount. According to Waring²⁷ such changes in electrical conductivity are not observed for carbon black in Neoprene and Perbunan, although softening as expressed by changes in dynamic stiffness is still obtained. Although not in any way conclusive, this does, in our opinion, throw more doubt on the assumption that change in chain structure is necessarily an important factor in the softening of rubber by stress under the experimental conditions considered here.

In order to make a further test of previous conclusions², an experiment was carried out on vulcanizates containing MPC black and HAF black. This formed part of a wider study designed to inquire how far the changes in stiffness due to stress are reversible by heating. In this experiment the procedure described earlier was used to obtain the variation of the parameters, G and μ , with prestress. This was done both for normal test-pieces and for test-pieces

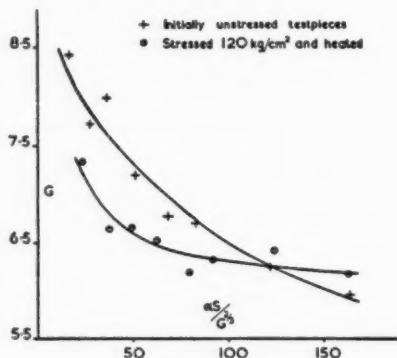


FIG. 21.—Partial reversibility of stiffness changes in MPC stock on standing and heating.

which had already been softened by stressing to 120 kg. per sq. cm., and then heated for 1 hour at 80° C and cooled. In addition the electrical resistivity of the test pieces was measured in the relaxed condition 5 minutes after the fourth extension. Contact with the rubber was made by means of aquadag and tin-foil. It should be emphasized that, owing to the large variability, the data from the electrical conductivity measurements are only approximate figures giving the order of magnitude. After stressing to 120 kg. per sq. cm., the resistivity of the vulcanize containing MPC black was approximately 2×10^{10} ohm-cm. Subsequent heating reduced the resistivity to approximately 5×10^9 ohm-cm., indicating that the heating has brought about some reformation of secondary chain structure. After applying a stress of only 30 kg. per sq. cm., the resistivity became approximately 2×10^{10} ohm-cm., which is the same as before heating. This indicates that the secondary structure reformed by heating is transient and can make no contribution to the stiffness at stresses exceeding 30 kg. per sq. cm. and may make no contribution even at much lower stresses. Similar results were obtained for the vulcanize containing HAF black; stressing to 120 kg. per sq. cm. increased the resistivity from about $3 \times$

10^3 to approximately 10^8 ohm-cm., and later heating reduced it to about 3×10^5 ohm-cm., indicating a substantial reformation of secondary chain structure. After subsequently applying the smallest stress of 30 kg. per sq. cm., the resistivity increased from 3×10^5 to approximately 10^7 ohm-cm. This is still less than the value before heating, but it does indicate that the reformed secondary chain structure contributes little to the stiffness at stresses exceeding 30 kg. per sq. cm. These results appear to confirm previous conclusions² that secondary chain structure is weak and makes little contribution to stiffness except, perhaps, at low stresses, and that the softening of rubber by applied stress is due almost entirely to rupture of carbon-rubber bonds and cannot be explained by breakdown of secondary chain structure.

RECOVERY OF STIFFNESS WITH STANDING AND HEATING

Mullins¹ has reported some recovery of stiffness with heating following the application of stress, and the present authors have obtained results which indicate a limited recovery. In Figure 21 G is plotted against $\frac{\alpha S}{G^{\frac{1}{2}}}$ for rubber containing MPC black and tested in the manner described in the previous para-

TABLE X
HAF BLACK VULCANIZATES

Pre-stress (kg./sq. cm.)	Modulus G		Extension factor μ		Electrical resistivity (ohm-cm.)	
	Stressed 120 kg./ sq. cm. and heated		Stressed 120 kg./ sq. cm. and heated		Stressed 120 kg./ sq. cm. and heated	
	Normal	heated	Normal	heated	Normal	heated
30	8.73	8.21	0.253	—	2×10^8	10^7
50	8.52	8.07	0.104	0.037	8×10^5	5×10^7
70	7.94	8.05	0.055	0.034	4×10^6	7×10^6
100	7.02	7.17	0.023	0.022	10^7	6×10^6
120	6.68	7.25	0.015	0.016	2×10^8	3×10^7
140	6.98	—	0.013	—	10^8	—
160	6.36	—	0.007	—	2×10^8	—

graph. Since the graph for the test-pieces which have been stressed 120 kg. per sq. cm. and heated is not a horizontal line, it would seem that a limited number of linkages have been formed and then broken by subsequent prestresses in the range 30 to 120 kg. per sq. cm. For the HAF black, there is also evidence of an appreciable recovery of stiffness in the heated test-pieces. This is shown in Table X, which includes data on electrical resistivity.

Electrical resistivity data obtained under the conditions of this experiment are variable and do not show any evidence of an increase in electrical resistivity with prestressing in the test-pieces which were initially stressed 120 kg. per sq. cm. and heated. Since these test-pieces soften appreciably with applied stress, the unchanged electrical resistivity is further evidence that the softening of reinforced rubber under the conditions of these experiments is not due to breakdown of secondary carbon chain structure.

NATURE AND PROPERTIES OF LINKAGES IN REINFORCED RUBBER

The application of Equations 17 and 19 has been facilitated by the discovery that K is the same, whatever the reinforcing filler. (Values of K obtained by

TABLE XI
VALUES OF K —EQUATION 16

Type filler and compound	K
MPC black (26 parts by vol.)	0.282
MPC black (heat-treated stock)	0.282
HAF black (26 parts by vol.)	0.270
Silene (26 parts by vol.)	0.272
Magnesium carbonate (26 parts by vol.)	0.272
P-33 black (36 parts by vol.)	0.290

applying Equation 16 are shown in Table XI.) This means that the proportion $\frac{dG}{G_r}$ of readily breakable linkages with any particular strength, X , is the same for all fillers tested. This striking result is not unexpected if the breakable linkages are interpreted as arising purely from physical adsorption of rubber molecules on the surface of the particles. It supports previous conclusions that the mechanism of softening is the same for each filler and is due to rupture of attachments between filler and rubber rather than to breakage of chain structure.

To facilitate calculations of $F(X)$, graphs of $F(X)$ against X were drawn taking the mean $K = 0.276$ from Table XI so that $F(X)$ could be read from the graphs. According to Equation 17 a plot of G against $F(X)$ should give a straight line of slope G_r and intercept G^* . Figures 22, 23, and 24 show the results which were obtained.

Since K is the same for all fillers the two quantities G^* and G_r obtained from these figures form a fairly complete description of the linkages present in the reinforced rubber. To give a more or less complete comparison of the stress-strain properties, however, it would be necessary to include μ , and this has not been attempted here. Table XII shows the values of G^* and G_r obtained in these experiments with the total G^* and G_r . In this table G^* , representing the strong linkages unbroken by stressing, includes of course the linkages due to vulcanization. Bearing this in mind, it will be appreciated that only a relatively small number of strong carbon-rubber linkages are present, but that

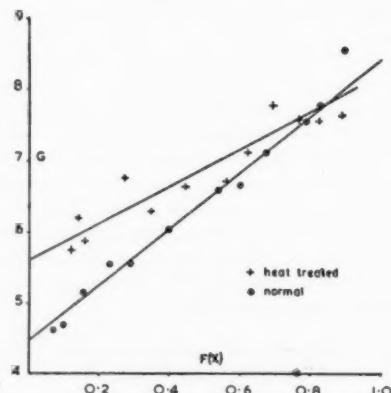


FIG. 22.—Relation between modulus and $F(X)$ for rubber containing 26 parts by volume of MPC black.

these are responsible for a marked stiffening of the rubber at high extensions. This confirms conclusions reached in an earlier paper²⁴ and is illustrated by the increase in μ , due to these strong linkages, which becomes very important at high extensions when the factor $(\alpha - 1)^4$ in the term $\mu(\alpha - 1)^4$ becomes large (Equation 10). Although the proportions of readily breakable linkages having various strengths is the same whatever the filler, *i.e.*, K is constant—the values of G , in the table show wide differences in the number of readily breakable linkages present in the rubber before stress is applied.

The distinction between G^* and G , is evidence that two types of linkage are present in reinforced rubber. The strong linkages responsible for G^* do not form part of the frequency distribution for the other linkages, and whereas the strong linkages are increased by heat treatment, the latter are reduced by it. This appears to be a clear demonstration that carbon black is responsible for two different types of linkage in reinforced rubber, and that this phenomenon

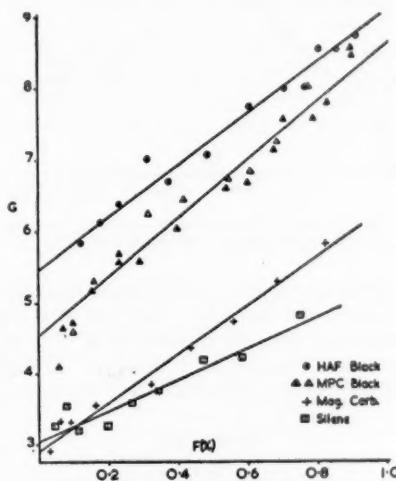


FIG. 23.—Relation between modulus and $F(X)$ for rubber containing 26 parts by volume of various fillers.

is particularly noteworthy with HAF black and with heat-treated rubber containing channel black. However, it is necessary to examine the possibility that the much greater number of strong linkages in heat-treated rubber and in rubber containing HAF black is due to chemical cross-linking between rubber molecules rather than to chemisorptive "cross-linking" through carbon particles. There is also the effect of carbon chain structure to be considered.

The high value of G^* for heat-treated rubber containing channel black cannot be explained by increased chain structure. In fact, the treatment increases the electrical resistivity from about 10^6 to 10^{12} ohm-cm., indicating that little primary or secondary chain structure remains. The increase in G^* takes place in spite of rather than because of changes in chain structure. It is equally impossible to explain the increase in G^* by direct chemical cross-linking between rubber molecules. A high-extension factor relative to modulus is characteristic of cross-linking by carbon particles (Table II), and this is, presumably be-

cause the cross-linking is by means of relatively large particles consisting of more than a few atoms. The heat treatment has increased the strong linkages, while greatly reducing the number of low and moderate strength linkages formed by carbon-rubber attachments. Hence if the increase in G^* is due to chemical cross-linking other than to linkages through carbon particles, the

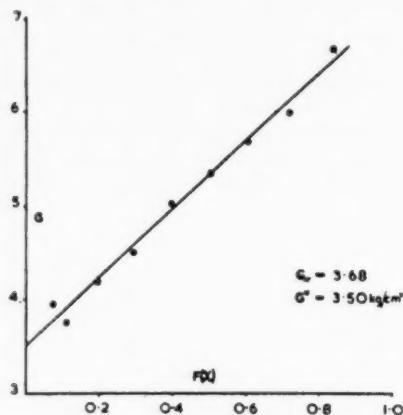


FIG. 24.—Relation between modulus and $F(X)$ for rubber containing 36 parts by volume of P-33 black.

extension factor should be greatly reduced by heat treatment. Figure 17 and Table IV show that this is not the case. In view of these considerations, it seems necessary to conclude that the increase in G^* due to heat treatment is caused by an increase in chemisorptive linkages through carbon particles formed at the expense of physical attachments. Such linkages would explain

TABLE XII
VALUES OF G^* AND G_r

Type of filler and compound	Modulus (G^*) due to strong linkages	Modulus (G_r) due to low and moderate strength linkages	Total ($G^* + G_r$)
HAF black (26 parts by vol.)	5.43	3.65	9.08
MPC black (26 parts by vol.)	4.50	4.14	8.64
MPC black (heat-treated stock)	5.60	2.58	8.18
Silene (26 parts by vol.)	3.01	2.20	5.21
Magnesium carbonate (26 parts by vol.)	2.90	3.40	6.30
P-33 black (36 parts by vol.)	3.50	3.68	7.18

the enormous increase in electrical resistivity which occurs during remilling of heat-treated stocks, since they would increase the forces developed during milling and hence cause breakage of carbon chain structure. This view is supported by recent unpublished work by the authors, which shows that a small quantity of sulfur in the heated stock leads to large increases in resistivity on

remilling after heating at temperatures and for times of heating which would otherwise have little effect. In this case the stock would be stiffened by a small number of vulcanization cross-links, and this would increase the forces developed during remilling.

Rubber containing HAF black shows little response to heat treatment (Table VI), except in electrical resistivity, which increases from about 10^3 to 10^4 to about 10^7 to 10^8 ohm-cm. This lack of response may be partly due to reduced primary chain structure counterbalancing increased numbers of strong carbon-rubber attachments. One difference between MPC and HAF blacks is the lower volatile content of the latter, and it may be that the lower susceptibility of HAF blacks to heat treatment is associated with this difference. Table XII shows that G^* for untreated rubber containing HAF black is as large as for the heat-treated MPC black stock. This large value is partly due to the greater degree of primary chain structure shown by the HAF black and the effect this will have on the number of linkages formed by carbon-rubber attachments. The high extension factors characteristic of cross-linking by carbon particles are also obtained for the HAF black, as shown in Table VIII. This indicates that the linkages responsible for the large value of G^* are formed through carbon particles or chains of carbon particles. Since these linkages do not form part of the strength distribution for the weaker linkages, it would seem that they also are the result of chemisorptive attachments. It appears that chemisorptive linkages form without a special heat treatment more readily with HAF than MPC black.

SIGNIFICANCE OF LINKAGES IN RELATION TO REINFORCEMENT

There is a wealth of information in the stress-strain curves of reinforced rubber, of which "modulus" as generally defined by the rubber technologist takes no account. The actual contribution to the experimentally measured stiffness of the linkages represented by G_r in Table XII depends on the stress applied and generally is considerable. (Indentation measurements which involve only low stresses are particularly affected by G_r , and this explains why heat-treated rubber is softer as judged by indentation.) If, however, the rubber is stretched until a tensile break occurs, all these linkages will have been broken during extension and so cannot contribute to tensile strength. On the other hand the strong linkages represented by G^* are likely to play a part in determining tensile strength. Some support for this view may be found in Table XII, which shows that G^* is low for the nonblack fillers and much higher for the fine particle size HAF and MPC blacks than it is for rubber containing a considerably greater volume of the comparatively large particle size P-33 black. However, the large increase in G^* in MPC vulcanizates following heat treatment is not accompanied by an increase in tensile strength, and the HAF black stocks with a high value of G^* have tensile strength no higher than those of MPC stocks. Therefore, other factors of importance in determining tensile strength are variables in these experiments or tensile strength tends to become independent of the number of strong linkages as the number of these linkages increases.

There is also some correlation between the strong linkages as represented by G^* and reinforcement as judged by abrasion resistance. For instance, abrasion resistance with nonblack fillers and with P-33 is known to be low when compared to MPC, and it is lower for MPC than for HAF black. An anomaly is again noticed with heat treatment which causes only a small increase in

abrasion resistance compared with a large increase in G^* . This apparently anomalous behavior may be at least partly accounted for by failure to take G_r into account. Unlike tensile strength it is quite possible that abrasive wear is affected by the low and moderate strength linkages responsible for G_r . If this is true, abrasion resistance should be influenced by prestressing the rubber before it is tested. Tests carried out on the Dunlop constant energy abrasion machine² indicated that the abrasion resistance of a vulcanizate containing 50 parts by weight of VFF (Statex K) black was reduced about 20 per cent by a 250 per cent prestretch. Subsequently experiments gave results (Figure 25) which show that considerable reduction in abrasion resistance, amounting to 30 per cent may be obtained by prestressing. Unlike the graphs showing the variation of G with prestress, these curves show no tendency to flatten as the prestress increases. This can be readily explained as follows. In contrast

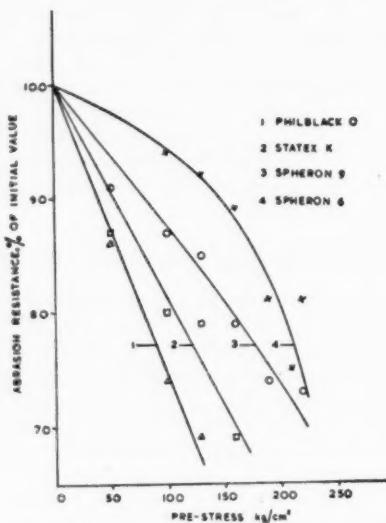


FIG. 25.—Influence of prestress on abrasion resistance.

with G , which clearly depends on the number of unbroken linkages and is independent of their strength (the margin by which they have escaped rupture is immaterial), abrasion resistance depends on both the strength and number of linkages. Hence, although the number of linkages broken at the higher prestresses is relatively small, the contribution which such linkages make individually to the abrasion resistance is relatively large (Figure 25), and the rate of diminution of abrasion resistance with applied stress does not decrease as the stress increases. The abrasion resistance appears to diminish more rapidly with applied stress in furnace blacks (curves 1 and 2) than it does for the channel blacks (curves 3 and 4). This is puzzling in view of the fact that $F(X)$ in Equation 17 is independent of the reinforcing filler. An interesting possibility which would tend to explain this is that good abrasion resistance may require a multitude of fine particles firmly attached to the rubber, and that the formation of linkages between rubber molecules is incidental but not essential to

improved abrasion resistance. If this is so, a contribution to abrasion resistance may be made by those particles or chains of particles which have only one firm attachment to the rubber and do not form a linkage (Figure 11). Such attachments make little contribution to the stiffness and are not so readily broken by applied stress. In order to explain Figure 25 it could, therefore, be argued that, owing to the slightly larger particle size and considerably greater degree of primary chain structure of the furnace blacks, a higher proportion of the physical attachments contributing to abrasion resistance form cross-linkages between rubber molecules and so may be readily broken by applied stress. The proportion of attachments which form cross-linkages increases with increasing particle size and primary chain structure because the surface area of the coherent units is then increasing, and this increases the probability of formation of the two or more attachments to any one unit necessary for the formation of a cross-linkage.

It appears that the low and moderate strength linkages represented by G_r make a contribution to abrasion resistance which cannot be ignored. It follows that one reason why the large increase in G^* due to heat treatment of rubber-channel black stocks (Table XII) does not lead to a correspondingly large increase in abrasion resistance may be found in the drastic reduction in G_r which accompanies this treatment. On the other hand, Table VII shows that G^* is considerably higher for HAF than for MPC black and G_r is less, but only slightly so. Hence it is not surprising that in this case markedly superior abrasion resistance is obtained.

GENERAL CONCLUSIONS

The results of this investigation strongly support previous conclusions by the authors² that the softening of reinforced rubber when it is stressed to moderate extensions owes little to breakdown of filler chain structure and is due primarily to rupture of attachments between the filler and the rubber molecules. This means that the stiffness of reinforced rubber is influenced greatly by the mode of attachment of filler to rubber, and the conclusion reached is that such stiffening by finely divided fillers is largely a consequence of linkages between rubber molecules formed through the filler particles by rubber-filler bonds and assisted by the presence of coherent chain structure of the filler particles themselves. The work further suggests that the linkages formed through carbon particles are of two kinds: one a relatively weak type linkage due to physical (van der Waals) attachments, the other a strong type linkage due to chemisorptive attachments which remain unbroken by stressing. The strong linkages are relatively few and have not been found with fillers other than carbon black, but the strength distribution of the weaker type does not depend on the chemical nature or type of filler, although differences are found in the total number of such relatively weak attachments.

The weak linkages are substantially all broken in the course of stressing to high elongations and the stiffening at the highest elongations is a consequence of the relatively small number of strong linkages. It is to be expected that among the fully reinforcing carbon blacks, where the particle sizes of the different types are roughly equivalent, those providing the greatest number of strong linkages will have the greatest reinforcing ability, and it may be significant in this connection that HAF black vulcanizates are recognized to have better abrasion resistance than MPC vulcanizates, in keeping with a larger number of strong linkages.

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CARBON BLACK DISPERSION AND REINFORCEMENT *

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The most generally recognized characteristic of a good reinforcing filler for rubber is small particle size. In the case of carbon blacks, numerous investigators have shown that reinforcement is enhanced as particle size decreases. As particle size cannot influence reinforcement unless the filler particles are dispersed or substantially wetted by the rubber matrix, it is necessary to investigate the importance of these factors.

Three possibilities exist as to the mode of dispersion of the filler in the rubber matrix. A most unlikely condition is conceivable, in which an ideal dispersion is obtained and each individual particle is separated from every other particle by a film of rubber. A second possibility is that aggregates of carbon black particles are present in the rubber and their size is proportional to the size of the individual particles. This would have to follow from the proved relationship of particle size to reinforcement. A third possibility is that the dominant factor in reinforcement is the extent of interfacial surface developed between the filler and the rubber phase. In this case, a highly aggregated and flocculated condition of the filler is not untenable with extensive development of interfacial surface. The correlation between particle size and reinforcement would be due to the direct relation between surface area and particle size.

A mechanistic explanation of the reinforcement phenomenon must be based on an understanding of the morphology of the carbon black-rubber system. This study has attempted to determine to what extent changes in the degree of dispersion are reflected in reinforcement, and the minimum degree of dispersion necessary for its development.

A single sample of a high-abrasion furnace black (HAF) was selected and used for preparing dispersion series in a variety of elastomers including "cold" GR-S, natural rubber, Butyl rubber, nitrile rubber, and Neoprene. A dispersion series containing easy-processing channel black (EPC) in cold GR-S was also studied. The recipes used for all the elastomers and the time and temperature of optimum cure are listed in Table I.

HAF BLACK-COLD GR-S DISPERSION SERIES

The results of the cold GR-S dispersion study are presented in some detail, followed by a discussion of the results of the studies in the other elastomers.

A laboratory Banbury was used to incorporate the black in the rubber, and the amount of mixing in the Banbury and subsequent roll-milling was adjusted to obtain various degrees of dispersion. The poorest dispersions were prepared by masticating the rubber and incorporating all the ingredients except the black

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in the Banbury; stopping the Banbury to add all the black; starting it again and lowering the ram as rapidly as possible; and dumping the batch as soon as the power consumption reached its maximum, indicating full incorporation. The minimum time necessary to incorporate the black was only 30 seconds in the case of cold GR-S and 50 parts of HAF.

The stock was passed once through a 12-inch roll mill to sheet it for curing. This stock was rough and dull in appearance, lacked green strength, and pieces

TABLE I

RECIPES

Cold rubber	Parts	Natural rubber	Parts
GR-S (× 558)	100	Smoked-sheet	100
Vulcan-3 (HAF) or EPC black	50	Vulcan-3 (HAF)	50
Zinc oxide	3	Zinc oxide	5
Stearic acid	1.5	Stearic acid	3
Agerite Hipar	1	Pine tar	3
Paraflex	5	Agerite Hipar	1
Circosol	3	Sulfur	2.8
Sulfur	1.75	Captax	0.5
Santocure ^a	1.25		

45 minutes at 292° F

^a 1.35 parts Santocure for EPC.

Butyl rubber	Parts	Nitrile rubber	Parts
GR-I-15	100	Hyear OR-25 EP	100
Polyac	0.3	Vulcan-3 (HAF)	50
Vulcan-3 (HAF)	50	Zinc oxide	5
Zinc oxide	5	Stearic acid	1.5
Stearic acid	0.5	Cumar P-25	10
Petrolatum	1.0	Dibutyl phthalate	10
Paraffin	1.0	Sulfur	2
Sulfur	2.0	Altax	1.5
Captax	0.5		
Methyl Tuads	0.75		

20 minutes at 300° F

Neoprene	Parts
Neoprene GN-A	100
Vulcan-3 (HAF)	40
Zinc oxide	5
ZLC magnesia	4.22
Stearic acid	0.70
Neozone-D	1.60
Permalux	0.50
Accelerator-552	0.26

10 minutes at 307° F

of unwetted black could easily be seen. Better dispersed vulcanizates were prepared by increasing the Banbury mixing times and rotor speeds. Heat treatment of cold GR-S black mixtures followed by remilling according to the well-known process of Gerke, Ganzhorn, Smallwood, and Howland¹ was also used in an attempt to prepare the best dispersions. In this case a black masterbatch of carbon black and rubber was prepared by Banbury mixing. The black masterbatch was heated in an oven for 1 hour at 170° C, allowed to age over-

TABLE II
HAF-COLD GR-S MIXING PROCEDURES

Mix no.	Banbury speed (r.p.m.)	Black mixing time (min.)	Maximum Banbury temp. (°F)	Milling	Remilling
1	77	0.5	185	1 pass	None
2	77	1.25	205	1 pass	None
3	77	4	230	1 pass	None
4	77	8	235	1 pass	None
5	77	4	230	5 min.	5 min.
6	77	2	260	5 min.	None
	113	4			
7	77	2	310	5 min.	None
	130	4			
8 ^a	77	2	300	1 pass	10 min.
	120	4			

^a Heat treated for 1 hour at 170° C.

night at room temperature, and remilled for 10 minutes, during which time the remaining ingredients were incorporated.

The mixing conditions of significance to this study are shown in Table II for the cold GR-S-HAF stocks. The stocks are listed in the order of increasing degree of mixing.

Table III lists the Mooney viscosities and stress-strain properties obtained at the optimum cure for this series of mixings.

An examination of the data for mixes 1 and 2 reveals the striking change in Mooney viscosity, tensile, hardness, and breaking elongation obtained by increasing the black mixing time from 30 seconds for mix 1 to 75 seconds for mix 2. The poor distribution of black in mix 1 and the presence of large lumps and aggregates are responsible for its low degree of reinforcement. The large change in Mooney viscosity with increased mixing shown by mixes 1, 2, and 3 probably results from the elimination of the high frictional resistance of contacting carbon aggregates. Negligible changes in Mooney viscosity, tensile strength, elongation, hardness, and modulus were found with increased mixing represented by mixes 3, 4, and 5. Mixes 6, 7, and 8 are characterized by the usual properties accompanying the development of high mixing temperatures. These effects are due to thermal changes in the base rubber, probably cross-

TABLE III
HAF-COLD GR-S RUBBER PROPERTIES

Mix no.	Com-pounded Mooney viscosity (ML, 4 min./212° F)	300% Modulus, (lb./sq. inch)	Tensile strength (lb./sq. inch)	Elonga-tion (%)	Hard-ness (Shore A2)
1	117	1630	1820	330	77
2	98	1600	3450	510	69
3	76	1740	3900	540	67
4	72	1710	3820	520	68
5	75	1600	3840	550	68
6	74	1900	3760	510	68
7	69	3140	3140	430	67
8	62	2200	3230	430	67

linking, chain scission, and the formation of carbon gel, which causes a rise in modulus, a drop in tensile strength and shorter breaking elongations. The modulus changes are insignificant as long as the temperature of mixing is not excessive. As a profound change in dispersion undoubtedly occurred over the entire range of mixing conditions, it is evident that static modulus is not sensitive to this factor. Also, it is apparent from the tensile data shown in Table III and the abrasion data in Table IV that modulus is independent of the reinforcement of these properties.

Table IV shows that the tear strength follows the same trends as tensile. Rebound and torsional hysteresis rapidly respond to increased mixing because of the reduction in carbon-carbon frictional losses as the dispersion is improved. Energy losses remain fairly constant for mixes 4, 5, and 6, and no large differences in dispersion can be inferred from these data. Mixes 7 and 8 show reduced energy losses, reflecting either or both the modulus increase discussed previously or a higher degree of dispersion. The angle-abrasion results are most striking. Except for mix 1, which was characterized by a most inferior dispersion, there was no real change in abrasion reinforcement over the remaining range of mixing conditions. It would almost seem that merely the incorpo-

TABLE IV
HAF-COLD GR-S RUBBER PROPERTIES

Mix no.	Tear strength (lb./inch)	Rebound (% R.E.)	Torsional hysteresis ($K \log$ decrement)	Angle abrasion (cc. loss / 10^4 rev.)	Electrical resistance (megohm-cm.)
1	213	54.8	0.284	742	0.0003
2	265	57.9	0.174	217	0.007
3	239	59.4	0.150	201	0.022
4	260	60.2	0.138	210	0.073
5	271	60.2	0.137	209	0.11
6	251	60.5	0.124	207	0.86
7	204	62.0	0.106	218	11,000
8	199	62.5	0.094	217	>60,000

ration and wetting of the black by the rubber phase during mixing are necessary for the full development of abrasion reinforcement. Additional mixing probably causes a more uniform distribution of the black aggregates throughout the rubber matrix, without any essential change in the size of the aggregates.

The electrical resistivity data in Table IV show the extreme sensitivity of this property to mixing variations. The same formulation in this case can give highly conducting vulcanizates if the mastication of the raw compounded stock is minimized, and on the other hand, give good insulating vulcanizates if high temperature mixing or black masterbatch heat treatment is employed. A popular explanation for the electrical conductive behavior of carbon black-loaded vulcanizates is that there are present through-going continuous or contacting chains of carbon black which act as conducting paths². Assuming this simple explanation, a decrease of electrical conductivity must result as dispersion improves and the conducting chains of black are broken. On this basis, the electrical resistance data indicate changes in dispersion with increased mixing. Recent work of Roth and McKinney³ of the National Bureau of Standards on electrical conductivity of carbon black-loaded vulcanizates has demonstrated that conductivity in cold GR-S is markedly influenced by the state of vulcanization, improving with increasing curative levels. These facts

are incompatible with the explanation of carbon black flocculation during cure, for flocculation should be retarded as the rubber matrix becomes more rigid as the cure proceeds, resulting in the opposite effect of decreasing conductivity with increasing curative levels. The analogous behavior of conductivity and strain data also suggests that the process of vulcanization has an important effect on both these properties. Perhaps the electrical characteristics of the rubber matrix and its interfacial contact with the carbon black surfaces also change during vulcanization. At least it is certain that the electrical conductivity of cold GR-S carbon black-loaded vulcanizates is a complex property which cannot be explained satisfactorily by assuming the presence of continuous paths of carbon.

MEASUREMENT OF CARBON BLACK DISPERSION

The electrical conductive and hysteresis properties of carbon black stocks can be used to rate the degree of dispersion in a relative and qualitative manner if the secondary factors influencing these properties are given consideration. A direct method of measuring dispersion is badly needed in order to establish a sound physical picture of the carbon black-rubber system on which to base the theories and assumptions necessary for an explanation of reinforcing action. Direct observation of microtomed rubber sections with the electron microscope has not been very successful because of the difficulty in obtaining specimens thin enough to give good resolution. Another method of judging the dispersion of carbon black in rubber is to dissolve the stock in a solvent and measure the amount of light transmitted at a given concentration of black¹. The solution of a rubber stock containing normal reinforcing loadings of black is extremely difficult, particularly if high temperatures or agitation are to be avoided so that the degree of aggregation of the black in the stock is not disturbed. Even with these precautions, the processes of swelling and solution may conceivably exert a dispersing action on the carbon black aggregates. The cold GR-S stocks described above were examined carefully by both a light transmittance method and electron microscope examination of films deposited from the same solutions used for the light transmittance measurements.

A number of difficulties had to be resolved before a satisfactory diluted and stable suspension of the original stock could be prepared for light transmittance measurements. Natural rubber or GR-S containing 50 parts of a good reinforcing black does not completely dissolve when immersed in benzene. A residue consisting of a swollen carbon black-rubber gel containing all of the black must be peptized to form a stable suspension. This can be partially achieved by heating and agitating the stock in a high boiling solvent. Such a procedure is far from satisfactory, and seriously limits the reliability of light transmittance methods.

The major objections to this procedure can be eliminated by using a 0.05 per cent solution of benzoyl peroxide in benzene as the solvent. No heating or agitation is required to peptize the gel and obtain a stable and well dispersed system. Systems containing 0.10 per cent of black were easily prepared from natural rubber or GR-S stocks by adding 100 cc. of 0.05 per cent benzoyl peroxide to the rubber stock and allowing the mixture to age for 24 hours at room temperature in the same type of extraction apparatus used for gel or bound rubber determinations. The 0.10 per cent black suspensions were too concentrated for light transmittance measurements and had to be diluted to 0.001 per cent. At this extreme dilution serious flocculation occurred, making it impossible to obtain reliable light transmittance values. In order to stabilize this

extreme black dilution, it was necessary to make the final dilution in a 0.2 per cent solution of the base rubber, and to use this same solution as the blank for determining the change in light transmittance caused by the carbon black. Thus, peptization of the black-rubber mix and stabilization of the final black dilution made it possible to study the effect of mixing on dispersion. A Beckman spectrophotometer, Model DU, was used to measure the light transmittance of the various suspensions. Table V lists the data obtained on the cold GR-S stocks whose preparation and rubber properties were described above.

These data indicate a very poor dispersion for mix 1, an intermediate state for mix 2, and a maximum state of dispersion for mixes 3 to 8. The maximum degree of dispersion is, therefore, rapidly achieved during Banbury mixing, as is evident from the large change in going from mix 1 to mix 2. The difference in mixing time between these stocks is only 45 seconds. The leveling off in light transmittance with mix 3 coincides with the development of full reinforcement in rubber properties. The fact that such large differences in aggregate size are at all evident after solution of the rubber stocks proves that the swelling and solution processes have at most a limited peptizing action. If this were not the case, the differences in aggregate size as judged from light transmittance would have been negligible.

TABLE V
HAF-COLD GR-S LIGHT TRANSMITTANCE

Mix no.	% Transmittance		
	4000 A.	5000 A.	6000 A.
1	82	83	84
2	39	44	47
3	32	36	41
5	32	36	41
7	31	36	40
8	32	36	41

Electron microscope examination of films cast from the dissolved stocks confirm the light transmittance results. Micrographs of the cast films shown in Figures 1 through 5 illustrate the poor dispersion of mix 1, and the more or less similar agglomerate size for mixes 2, 3, 7, and 8. The stock which had the greatest amount of mixing, mix 8, shows the presence of large agglomerates and stable aggregates. The stable aggregates can be differentiated from the looser agglomerates because of a characteristic peculiarity of the type of aggregation observed for oil-type furnace blacks. Electron micrographs of oil blacks always show chain-like aggregates built up from units of the same size, never a chain of particles consisting of a mixture of individual sizes. The fact that groupings of uniform particle size are clearly observable after incorporation in rubber and dissolving of the stocks is definite evidence that no dispersion of these stable aggregates has occurred, and that they have not been formed by flocculation after mixing with rubber.

CHANNEL BLACK DISPERSION SERIES IN COLD GR-S

The preceding study was repeated with easy-processing channel black replacing the high abrasion furnace black. The mixing procedures are listed in Table VI, rubber properties in Tables VII and VIII, and the light transmittance values for 0.001 per cent black suspensions in Table IX. The rate of tensile strength development as mixing is increased, shown in Table VII, the gradual

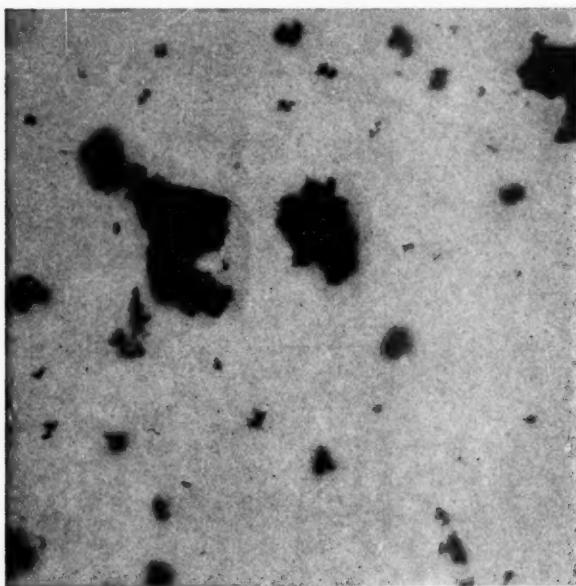


FIG. 1.—Cast film specimens of mix 1 (14,000 X). Vulcan 3 in GR-S (X558).

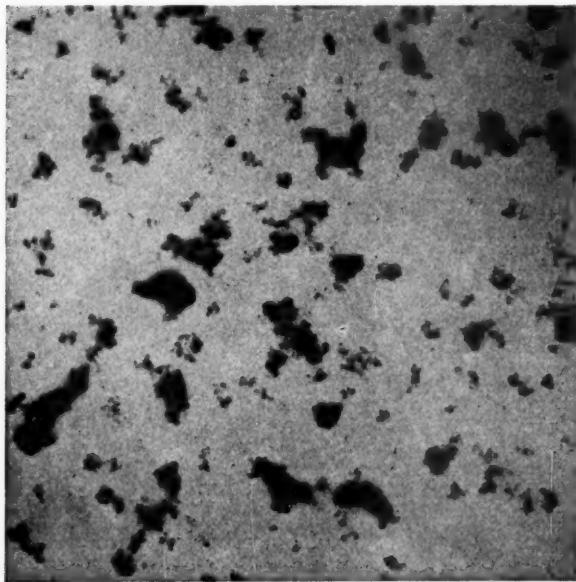


FIG. 2.—Cast film specimens of mix 1 (14,000 X). Vulcan 3 in GR-S (X558).

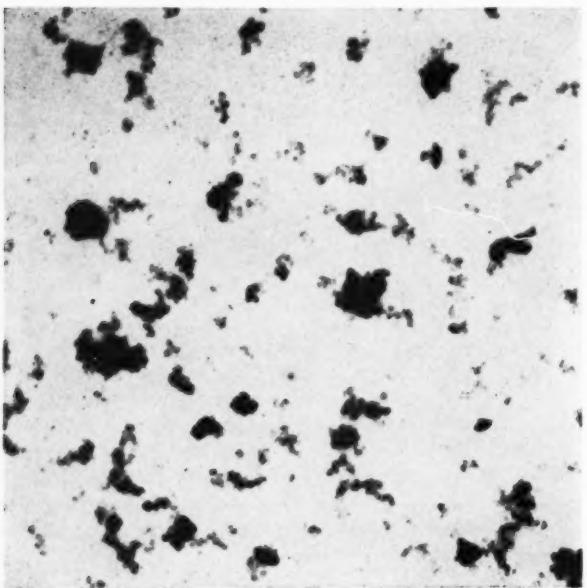


FIG. 3.—Cast film specimens of mix 3 (14,000 \times). Vulcan 3 in GR-S ($\times 558$).

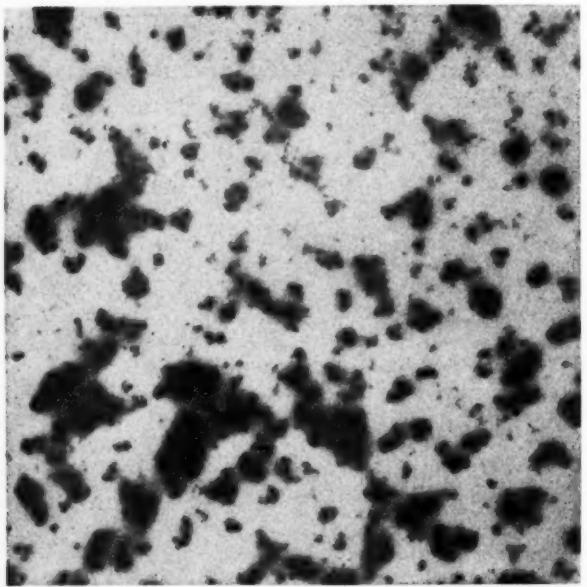


FIG. 4.—Cast film specimens of mix 7 (14,000 \times). Vulcan 3 in GR-S ($\times 558$).

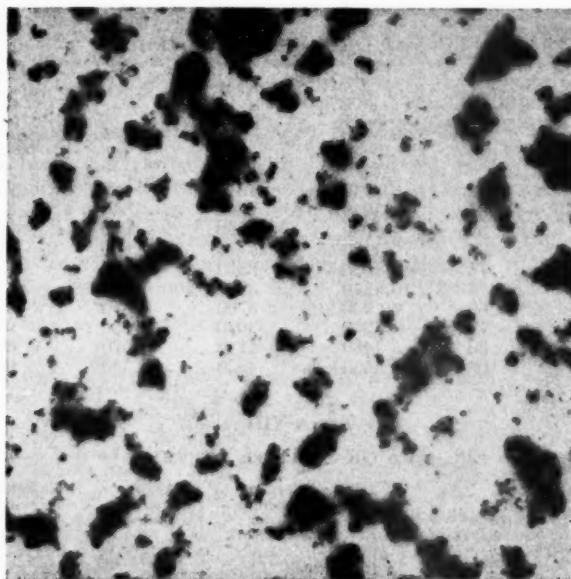


FIG. 5.—Cast film specimens of mix 8 (14,000 X). Vulcan 3 in GR-S (X558).

improvement in abrasion resistance, shown in Table VIII, and the somewhat slower approach to minimum light transmittance values, shown in Table IX compared to the results obtained in the HAF series, indicate the possibility that channel black is somewhat more difficult to disperse than HAF black. This has been suggested by Dannenberg, Jordan, and Stokes⁴. Judging from tensile strength and abrasion results, it appears that these properties improve with increased mixing and begin to level off after 4 minutes of Banbury mixing with

TABLE VI
EPC-COLD GR-S MIXING PROCEDURE

Mix no.	Banbury speed (r.p.m.)	Black mixing time (min.)	Maximum Banbury temp. (° F.)	Milling	Remilling
1	77	0.33	188	1 pass	None
2	77	0.75	196	1 pass	None
3	77	1.25	209	1 pass	None
4	77	2	218	1 pass	None
5	77	4	230	1 pass	None
6	77	8	238	1 pass	None
7	77	8	243	5 min.	5 min.
8	77	1.5	263	1 pass	None
	113	6			
9	77	1.5	305	5 min.	None
	130	6			
10 ^a	77	1.5	305	None	10 min.
	130	6			

^a Masterbatch heat treated for 1 hour at 170° C.

TABLE VII
EPC-COLD GR-S RUBBER PROPERTIES

Mix no.	Compounded Mooney viscosity, (ML, 4 min./212° F)	300% modulus, (lb./sq. inch)	Tensile strength (lb./sq. inch)	Elongation (%)	Hardness (Shore A2)
1	108	940	1310	380	75
2	98	1040	2460	550	73
3	92	1040	3320	650	70
4	86	1120	3440	640	69
5	78	1020	3350	640	67
6	73	1140	3800	660	68
7	69	940	3700	670	67
8	73	1240	3670	600	66
9	69	1480	4140	570	66
10	68	1550	4330	550	66

TABLE VIII
EPC-COLD GR-S RUBBER PROPERTIES^a

Mix no.	Tear strength (lb./inch)	Rebound (% R.E.)	Torsional hysteresis (K log decrement)	Angle abrasion (cc. moss/10 rev.)	Electrical resistance (megohm-cm.)
1	259	56.3	0.321	838	15
2	352	56.2	0.283	529	78
3	307	55.0	0.287	414	43
4	322	54.5	0.296	386	70
5	319	55.6	0.274	355	84
6	322	55.4	0.264	323	116
7	271	55.8	0.250	323	290
8	283	56.1	0.249	321	261
9	266	59.1	0.150	281	>60,000
10	238	61.1	0.107	273	>60,000

^a 1.35 parts Santocure.

TABLE IX
EPC-COLD GR-S SERIES

Mix no.	% transmittance		
	4000 A.	5000 A.	6000 A.
1	73.2	86.2	90.2
2	52.5	64.3	69.8
3	47.0	53.0	59.2
5	28.2	37.0	45.9
6	29.6	37.2	44.5
7	29.5	37.7	46.2
8	27.6	36.1	43.8
9	28.4	37.0	45.0
10	26.9	35.3	44.5

the HAF stocks and 8 minutes with the EPC stocks. However, in both cases, by far the major reinforcing effect is obtained after only 1.25 minutes of Banbury mixing.

The performance of the channel black stocks differed from that of the HAF stocks under conditions of high-speed, high-temperature Banbury mixing, and heat-tempering of the masterbatches. In the case of the HAF stocks, a drop

in tensile strength and no appreciable improvement in abrasion resistance were obtained, whereas the EPC stocks gave improved tensile and abrasion properties. The trends of other properties in the EPC series were similar to those observed for the HAF series.

MIXING VARIATIONS IN NATURAL RUBBER

The response to variations in mixing of a natural-rubber tread compound containing 50 parts of HAF black was studied, following the same techniques used for cold GR-S. Table X shows the mixing procedures used, and Tables XI and XII list the rubber properties for the various stocks. High-speed Banbury mixing caused the development of high temperatures, which had a striking influence on rubber properties. Mixes 1, 2, and 3 have essentially the same

TABLE X
NATURAL RUBBER MIXING PROCEDURES

Mix no.	Banbury speed (r.p.m.)	Black mixing time (min.)	Max. Banbury temp. (° F.)	Milling	Remilling
1	77	1.1	210	1 pass	None
2	77	4	255	1 pass	None
3	77	4	260	5 min.	5 min.
4	77	2	320	3 min.	None
	116	4			
5	77	2	355	3 min.	None
	131	4			
6 ^a	77	2	260	7 min.	5 min.
	131	4			

^a Additional 1-hour heat treatment at 170° C.

TABLE XI
NATURAL RUBBER PROPERTIES

Mix no.	300% modulus (lb./sq. inch)	Tensile strength (lb./sq. inch)	Elongation (%)	Hardness (Shore A2)	Rebound (% R.E.)	Torsional hysteresis (K log decrement)	Permanent set 60-min. cure
1	2170	3790	470	69	65.9	0.196	25
2	2220	3750	460	68	66.5	0.164	24
3	2100	3880	460	66	68.8	0.152	25
4	2460	3670	400	64	72.6	0.083	17
5	2550	3600	400	63	72.8	0.073	16
6	2430	3350	380	63	72.2	0.082	16

TABLE XII
NATURAL RUBBER PROPERTIES

Mix no.	Electrical resistance (megohm-cm.)	Angle Abrasion, (cc. loss 10 rev.)	Tear strength (lb./inch)	De Mattia cut growth (kc. to 1 inch)
1	<0.002	354	613	125
2	<0.002	327	636	275
3	<0.002	328	281	490
4	0.77	273	166	500
5	17	274	156	520
6	4	263	152	75

rubber properties and indicate that a really poor dispersion of carbon black in natural rubber could not be prepared. This is most unexpected, considering the fact that mix 1 had a total mixing time of slightly over 1 minute, which was the minimum time required barely to incorporate the black in the rubber. High temperature mixing represented by mixes 4, 5, and 6 caused an increase in modulus, lower tensile strength, shorter breaking elongations, lower hardness, lower hysteresis losses, lower permanent set, increased abrasion resistance, lower tear strength, and a very large increase in electrical resistance. These changes have been attributed to improved dispersion of carbon black, thermal breakdown, oxidative cross-linking of the rubber, and the formation of a carbon black-rubber gel complex. Light transmittance measurements on solutions of the stocks indicate that no essential change in the size of the dispersed aggregates has occurred over this range of mixing conditions.

These results indicate that changes in the rubber matrix are responsible for the effects produced by high-temperature mixing and heat treatment.

It would seem from this study that the process of incorporation of carbon black in natural rubber is accompanied by a concurrent process of rapid wetting and distintegration of carbon aggregates. Once this has occurred, further mixing does not appear to have a significant effect on aggregate size. Electron microscope studies of the least and most energetic mixings have shown them to be almost identical. The definite difference in the visual appearance of the stocks prepared using these two extremes in mixing must be due to the presence of a small percentage of the total black, since large lumps which do not seriously detract from the reinforcing function of black that is well incorporated. The electrical resistance change due to high-speed mixing is similar to results obtained in cold GR-S.

BUTYL RUBBER MIXING STUDY

The use of different mixing conditions for a GR-I-15 formulation containing 50 parts of HAF black did not result in any appreciable changes in cured rubber properties. However, a noticeable decrease in Mooney viscosity is obtained with increasing amounts of mixing. In general, the results obtained parallel those in natural rubber, except that the exceptional thermal and oxidative stability of Butyl rubber prevented the changes due to high temperature mixing and heat treatment which were observed for natural rubber and cold GR-S.

TABLE XIII
NITRILE RUBBER MIXING PROCEDURES

Mix ^a no.	Gum roll mill ^a pre- mastication (min.)	Banbury speed (r.p.m.)	Black mixing time (min.)	Maxi- mum Banbury temp. (° F.)	Milling (min.)	Remilling (min.)
1	25	77	1	240	None	1
2	25	77	2	255	None	1
3	10	77	4	250	8	None
4	10	77	2.5	275	8	5
		120	5			
		130	1			
5 ^b	10	77	2.5	335	None	5
		116	6			

^a Mixes 1, 2, and 3 were fully compounded except for black and premasticated. For mixes 3, 4, and 5 gum was premasticated before adding to Banbury.

^b Masterbatch heat treated 1 hour at 170° C before remill.

TABLE XIV
NITRILE RUBBER PROPERTIES

Mix no.	200% modulus (lb./sq. inch)	Tensile strength (lb./sq. inch)	Elongation (%)	Hardness (Shore A2)	Rebound (% R.E.)	Angle abrasion (cc. loss/10 rev.)	Strength (lb. inch)	Electrical resistance (megohm-cm.)
1	1690	1960	230	77	50.7	404	183	0.003
2	1680	2400	250	77	52.4	380	193	0.003
3	1930	2890	260	76	51.6	366	178	0.007
4	2010	3010	240	76	52.1	336	185	0.24
5	2070	2950	240	76	51.5	350	147	0.35

There is no real indication from the rubber properties that any substantial change in carbon black dispersion was effected by increased mixing. Considering the extreme range of mixing conditions used in this study, it is again remarkable that essentially full reinforcement is developed by an amount of mixing which is just about capable of incorporating the carbon black.

Tables XIII and XIV list the mixing schedules and rubber properties for the nitrile rubber study.

Nitrile rubber loaded with 50 parts of HAF black shows a rapid tensile response with increased mixing, similar to the behavior of cold GR-S. Tensile strength would be expected to respond to dispersion changes in the case of nitrile rubber, as its pure-gum tensile properties are in the same class as GR-S. In other properties, nitrile rubber seems to be rather insensitive to mixing variations. High-temperature mixing and heat treatment effect a very small change in properties, and it is this property of heat resistance which makes nitrile rubber such an outstanding industrial product. The large change in electrical resistance for mixes 4 and 5 is in itself of practical interest, but it does not indicate any change in reinforcement.

The effect of mixing variations on the rubber properties of a Neoprene stock containing 40 parts of HAF black was investigated. The mixing conditions and rubber data obtained are shown in Tables XV and XVI. High-temperature, high-speed Banbury mixing, and heat treatment which were used in the previous studies could not be employed with these Neoprene stocks because of scorching difficulties. For mixes 1, 2, 3, and 4, all ingredients except the black were incorporated during roll milling, and this base stock and the black were then Banbury-mixed for times ranging from 0.5 to 5 minutes. Mixes 4 and 5 were Banbury-mixed for 5 minutes followed by remilling for 10 and 20 minutes, respectively.

TABLE XV
NEOPRENE TYPE GN-A MIXING PROCEDURES

Mix no.	Premastication (min.)	Black mixing time (min.)	Maximum Banbury temp. (° F.)	Milling	Remilling
1	20 ^a	0.50	166	1 pass	None
2	20 ^a	0.75	158	2 passes	None
3	20 ^a	2	188	1 pass	None
4	20 ^a	5	216	1 pass	None
5	15 ^b	5	226	None	10 min.
6	15 ^b	5	241	None	20 min.

^a Premastication on cold, tight mill used to incorporate all ingredients except black.

^b All ingredients added except black and zinc oxide. Zinc oxide added on remill after aging 24 hours.

The data shown in Table XVI are rather difficult to interpret because they are at variance with the results obtained in the previous studies. The effects associated with high-temperature mixing with the other rubbers, such as lower Mooney viscosity values, lower hardness, and lower tensile strength, were not obtained with this series of Neoprene stocks. The increase in viscosity with increased mastication is probably due to the tendency of Neoprene to cross-link or "set up" on exposure to the elevated temperatures developed during mixing. Improved carbon black dispersion and increased mastication would normally have the opposite effect on viscosity. The cross-linking of Neoprene during processing has a different effect on rubber properties than the changes usually associated with high-temperature mixing and heat treatment, because temperature conditions were low enough so that chain scission did not occur. In both cases, cross-linking causes an increase in stiffness. It is felt that in the case of Neoprene, the gradual improvements in tensile strength rebound, and abrasion with increased mixing are due to improvements in carbon black dispersion.

TABLE XVI
NEOPRENE TYPE GN-A RUBBER PROPERTIES

Mix no.	Com-pounded Mooney viscosity (ML 4 min./212° F.)	300% modulus, (lb./sq. inch)	Tensile strength (lb./sq. inch)	Elonga-tion (%)	Hard-ness (Shore A2)	Rebound (% R.E.)	Angle abrasion (cc. loss/10 rev.)	Electrical resistance (megohm-cm.)
1	87	2560	2730	310	81	59.4	501	<0.001
2	85	2500	3300	390	80	59.7	440	<0.001
3	97	2730	3800	410	80	61.8	407	<0.001
4	>100	3200	3780	370	81	63.1	427	0.009
5	99	3400	3980	350	80	66.2	421	0.023
6	>100	3320	4100	350	81	66.6	394	0.46

Previous work by Dannenberg, Jordan, and Stokes⁴ on the effect of cross-linking Butyl gum by heat treatment with Polyac prior to incorporating carbon black has shown similar trends in rubber properties with increased Polyac cross-linking. Definite improvements in carbon black dispersion were achieved by increasing the elasticity or nerve of the Butyl gum and thus providing greater shearing or grinding action. The slight cross-linking of Neoprene during prolonged mixing is apparently comparable to the Polyac heat treatment of Butyl rubber, and results in similar improvements in carbon black dispersion. This property of Neoprene makes it unique among the other rubbers, because it allows a continually improving dispersion as mixing progresses. The more unyielding the carbon black aggregates become to further disintegration, the tougher the rubber matrix gets to do the job.

The electrical resistivity data show the expected trend with improved dispersion, but again it is questionable whether dispersion is the only factor involved.

SUMMARY

Different mixing conditions were employed to obtain vulcanizates, varying only in degree of carbon black dispersion, with natural and synthetic rubbers, using a single sample of a commercial grade HAF black. Light transmittance measurements on dilute solutions of dissolved unvulcanized stocks prepared by an improved technique were used to evaluate the size of carbon black aggre-

gates in cold GR-S and natural rubber stocks. Electron micrographs of films show the high degree of carbon black aggregation, even after prolonged mixing. A limiting degree of dispersion or a minimum aggregate size is obtained very rapidly as mixing is increased. Black incorporation and dispersion appear to take place simultaneously; a high degree of abrasion reinforcement was noted in most rubbers with mixing (less than 75 seconds) barely sufficient to incorporate the black. Carbon blacks in general respond rapidly to mixing, and the chainlike aggregates characteristic of reinforcing carbon blacks observed under the electron microscope are practically unchanged after mixing with rubber. Dispersion of carbon blacks during mixing depends on the packing and coherence of their agglomerates resulting from such factors as surface oxidation and extent of mechanical bulk densification. There is some evidence that oil-type furnace blacks disperse more easily than channel blacks. A major cause of the disappointing abrasion reinforcement with most noncarbon pigments possessing extreme fineness may be the tendency for excessively strong aggregate binding and resulting large aggregates in rubber. A striking rise in electrical resistivity was observed as the amount of mixing was increased. As the size of the aggregates did not change, the higher electrical resistivity cannot be explained by assuming better dispersion and breakdown of conductive carbon paths. Increased mixing might provide better distribution of the carbon aggregates in in the rubber matrix without change in size of aggregates.

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SOME PROPERTIES OF BUTYL RUBBER-CARBON BLACK SYSTEMS*

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The effect of varying milling conditions on several specific properties of Butyl rubber-carbon black systems has been discussed in a previous paper¹. In that work, it was shown that changes in mill roll clearances had a pronounced effect on the dispersion of SRF furnace black in Butyl rubber. The differences in dispersion were observed by means of the electron microscope and by photometric and plastometric methods. The relative size of SRF black agglomerates in different compositions was compared by examination of dilute suspensions in a photometer. Electron micrographs (Figure 1) were prepared from similar suspensions. The bulk viscosity was determined on carbon black masterbatches with a parallel plate plastometer². These data are summarized in Table I.

A continuation of the study of these systems has brought forth new information on the relationship of carbon pigments to Butyl polymers. Such data have been obtained by more detailed photometric and plastometric measurements. These techniques revealed changes taking place in Butyl-SRF systems

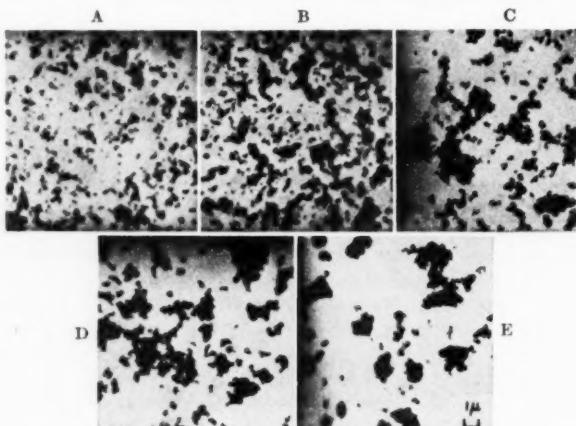


FIG. 1.—Electron micrographs of Butyl rubber-carbon black dispersions.

- A. 0.010-inch mill setting
- B. 0.021-inch mill setting
- C. 0.034-inch mill setting
- D. 0.059-inch mill setting
- E. 0.068-inch mill setting

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TABLE I
CARBON BLACK DISPERSIONS
50 parts SRF in GR-I-15

Mill setting (inch)	Light transmittance ^a (%)	Average agglomerate size (micron)	Viscosity ($\times 10^{-4}$ poises)
0.010	20	0.17	39.6
0.020	25	0.26	47.9
0.035	57	0.35	54.6
0.050	53	0.39	51.3
0.070	60	0.46	69.2
GR-I-15, not milled			20.9
GR-I-15, milled 7 minutes, 0.010-inch setting			19.2
GR-I-70, not milled			54.5

^a 0.0068% solution.

on exposure at different temperatures before vulcanization. The influence of vulcanizing conditions on the pigment habit of these systems was also investigated. In this work extensive use of electrical resistivity measurements was made. Viscosity tests on unvulcanized systems as well as conventional stress-strain measurements of the vulcanizates were also employed.

Most of the present study was devoted to two systems—fine dispersions prepared on an 0.010-inch mill, and gross dispersions prepared on an 0.070-inch mill. The practical effect of dispersion differences obtained from such variations in mixing conditions is illustrated in Figure 2. Analysis of changes taking place in such systems under a variety of conditions has led to the conclusion that the existence of some form of association between polymer and pigments is quite probable.

PHOTOMETRIC STUDIES

The further study of SRF-Butyl rubber systems in the unvulcanized state was undertaken to investigate a certain apparent lack of reproducibility in the photometric test. It was discovered, for example, that the light transmittance values of suspensions of a given set of compounds, prepared at different times, were variable. At first it was thought that these differences were attributable to changes in solvent or in the technique used in the preparation of the suspensions. Chemical analysis of the solvents eliminated the first possibility. While it was determined that the time and vigor of agitation employed in making the

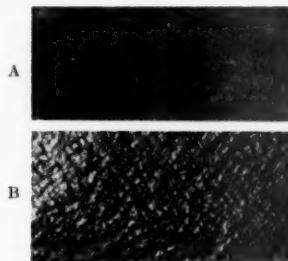


FIG. 2.—Calendered Butyl compositions.
A. Fine dispersion, 0.010-inch mill setting
B. Coarse dispersion, 0.070-inch mill setting

suspensions had some effect on their opacity, the observed differences could not be entirely accounted for in this way. A change in particle configuration or bound rubber content was suspected. A number of experiments were performed to investigate such possibilities. In each case a fine dispersion (0.010-inch mill setting) and a gross dispersion (0.070-inch mill setting) were made.

Suspensions were prepared by weighing a 0.5-gram sample on an analytic balance. A quantity of solvent, equivalent to 50 cc. of solution per 0.5 gram of compound, was measured out in a buret. Either heptane or cyclohexane was used. Although cyclohexane is a more powerful solvent for Butyl, in dilute suspensions identical photometric readings were obtained with either solvent. The samples of compound and the solvent were placed in 2-ounce square transparent bottles with tight fitting screw-type plastic caps. The bottles were then placed on a slowly revolving wheel for approximately 16 hours. The wheel had a maximum diameter of 13 inches and revolved approximately once every 1.5 minutes. Under these conditions a freshly prepared Butyl-SRF dispersion gave uniform homogeneous suspensions. These 1 per cent suspensions were carefully diluted to 0.01 per cent concentration, and

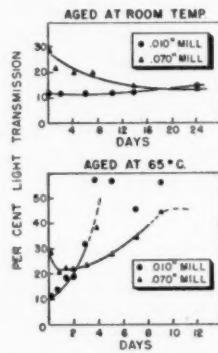


FIG. 3.—Drift in light transmittance of SRF-Butyl compounds.

light transmittance values were obtained on the Diller colorimeter, using calibrated test-tubes as the sample holder. In repeated tests, the fine dispersion gave a value of from 12 to 14 per cent light transmitted, while the gross dispersion had readings of from 29 to 32 per cent light transmitted. Several different batches of such dispersions were allowed to age both at room temperature and at 65° C before being placed in suspension in cyclohexane. Readings were obtained on such samples at various exposure times. The results of several experiments are shown in Figure 3. It is evident that the large clumps of black in the coarse dispersion had undergone some change in their configuration on standing at room temperature. After several weeks it apparently has undergone an improvement in dispersion. Actually this is not the case, as will be shown, but certainly some change has taken place.

A more marked reaction evidently occurs at 65° C, as might be expected. The fine dispersion shows a relatively rapid increase in light transmittance value, while initially the gross dispersion undergoes a decrease in value. An explanation for this phenomenon is that bound rubber formation is taking place. In a fine dispersion this can occur immediately as soon as proper condi-

tions are provided, specifically increased temperature. A coarse dispersion, however, must first undergo some change in its configuration, so that subsequent polymer "wetting" or insolubilization may take place. Hence, an initial increase in opacity of the dilute suspensions—decreased light transmittance—is explainable on the basis of a reduction in particle size. This decrease in size, then, permits bound rubber to form more readily.

The evidence for bound rubber formation is sound enough, but as yet it has not been possible to place it on a quantitative basis for Butyl-SRF systems. As a Butyl-SRF compound ages it gradually develops signs of insolubility, whereas a fresh mixture yields a homogeneous suspension, in which discrete particles can be observed only microscopically. An aged composition produces coarse suspensions, in which large specks of composition are quite visible to the naked eye. These clumps are essentially insoluble and, in time, comprise the major portion of the suspensions. Under such conditions, photometric analysis becomes quite inaccurate and of little value in the study of such phenomena.

Determination of the bound rubber content of Butyl-SRF systems might be made by other methods. Diffusion methods employing dialysis sacs made

TABLE II
EFFECT OF AGING ON VISCOSITY

Aging conditions	Viscosity $\times 10^{-6}$ poises	
	0.010-inch mill	0.070-inch mill
Original	43.1	72.0
16 hr. at 65° C	42.3	76.3
48 hr. at 65° C	—	73.4
92 hr. at 65° C	50.7	79.8
116 hr. at 65° C	52.6	86.4
7 days at 65° C	53.7	85.5
9 days at 65° C	53.2	—
20 days at 65° C	54.0	85.2
5 wks. at room temp.	48.4	80.4
8 wks. at room temp.	47.1	80.4

of pure-gum Butyl vulcanizates have been suggested by an associate. On the other hand, channel black forms very tight gel structures with Butyl, and the determination of the bound rubber content of such systems is quite simple and reproducible. A technique similar to that suggested by Sperberg and his associates³ has been found to be a convenient method of measuring the bound rubber content of unvulcanized Butyl-channel black systems. Unfortunately carbon gels produced by furnace blacks in Butyl are not stable enough for determination by this method. Possibly a modified procedure, based on polar solvents or lower temperatures, would be feasible.

It might be concluded from the photometric work described above that aging of Butyl-SRF mixtures brings about a definite improvement in dispersion. Such a view would be based on the fact that the polymer is gradually made insoluble, or adsorbed, by the pigment. However, in previous work¹ it was shown that differences in dispersion, *i.e.*, differences in degree of agglomeration, could be detected by plastometric measurements. Therefore, parallel-plate viscosities were obtained on the compositions which had been aged at 65° C. Both the fine and coarse dispersions showed a slight gradual increase in viscosity on aging at this temperature (Table II). Had a significant improve-

ment in dispersion (agglomerate disaggregation) occurred, a lower viscosity would have been expected. On the other hand, the increase in viscosity was not sufficient to indicate any considerable increase in agglomerate size.

The present authors offer the following explanation for these phenomena. A change in dispersion occurs principally through severe mechanical working of a mix. Under static conditions there is no reason to suppose a movement of carbon particles either in building up or reduction of agglomerate structures⁴. What apparently does take place is a gradual sorption of polymer and pigment. Presumably, such association takes place whether the carbon particles are discrete or in agglomerates.

Admittedly this analysis does not take into account possible thixotropic effects. A thorough investigation of such factors should be made. Unfortunately, this is beyond the scope of the present paper. However, viscosity determinations on pure-gum Butyl before and after milling (Table I) and on pigmented systems over varying periods of time do not support the thought that thixotropic effects are a dominant factor in these systems.

ELECTRICAL RESISTIVITY MEASUREMENTS

Since it has already been shown that the degree of dispersion of carbon particles may vary considerably, it is reasonable to expect that such differences may have an influence on electrical resistivity. A number of investigators⁵ have utilized this effect in studying carbon black dispersion. Usually, however, such work has been confined to vulcanized systems. In the present investigations, particular emphasis has been placed on resistivity measurements of unvulcanized compositions. These determinations were made in a conventional manner, using a guarded ring electrode and a weighted electrode. The specimens were approximately $6 \times 6 \times 0.075$ inches in size, and were covered on one side with 0.001-inch aluminum foil before testing. A maximum charge of 540 volts, supplied by dry batteries was used in this work.

Samples were prepared for resistivity measurements either by calendering or by molding in a $6 \times 6 \times 0.075$ inch tensile pad-mold. The temperatures and pressures at which these operations were performed had an important bearing on resistivity and will be discussed. In view of photometric and plastometric data, it is of interest to consider the resistivity of fine and coarse dispersions and the effect of aging on this property in the unvulcanized state.

It was readily demonstrated that fine dispersions had a relatively high resistivity, 10^{14} ohm-cm., while coarse dispersions were in the range of 10^8 to 10^9 ohm-cm. specific resistivity. These effects were quite reproducible. The effects of aging on such systems are shown in Figure 4. The most conspicuous change noted was the increase in resistivity of the gross dispersion. This approaches the value obtained on a well-dispersed system. A second phenomenon which seems to be a reproducible one is that the resistivity of a good mixture shows a slight initial drop which is followed by a recovery to a higher level, near the limit of instrumental accuracy. The resistivity values are slightly higher for a specimen which has been subjected to test on several occasions than for another specimen of the same composition which rested for 17 days with no tests. In all cases the resistivity is in the order of 10^{13} to 10^{14} ohm-cm. When aged at $65^\circ C$, the resistivity values converge more rapidly and come to equilibrium at about 10^{10} ohm-cm. All these changes are consistent with the light transmittance effects described earlier.

Two obvious differences exist between resistivity of raw compounds and

vulcanizates of identical composition. Raw compounds come to equilibrium at 10^{10} or 10^{14} ohm-cm., depending on temperature, while cured specimens have a specific resistivity of 10^7 or 10^8 ohm-cm., at the highest. The other distinction is that unvulcanized samples show a pronounced drift in electrical resistivity during exposure to an electrical potential, while vulcanizates are quite stable in this respect. The effect of electrical field on viscosity is shown in Table III. The magnitude of electrical drift in uncured compounds is quite striking, as seen

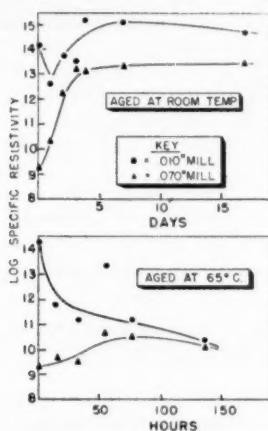


FIG. 4.—Drift in electrical resistivity of SRF-Butyl systems.

in Figure 5. This plot indicates the drift observed in a compound subjected to a constant electrical potential for a period of about 27 hours. A change in resistivity from $>10^{14}$ at the start to $<10^8$ ohm-cm. was recorded after 24 hours under the constant imposition of an electrical potential. This suggests some form of particle alignment induced by the current. However, the effect on the viscoelastic flow properties of the compound is negligible, indicating that any new alignment which may have been set up was comprised of weaker forces

TABLE III
EFFECT OF ELECTRICAL FIELD ON VISCOSITY

Dispersion	$\eta \times 10^{-4}$ poises
Fine, 0.010 inch	44.0-45.7
Coarse, 0.070 inch	71.3-73.6
Coarse, molded, control	57.7-63.7
Coarse, molded, tested for resistivity drift	54.1-56.4

than those obtained in the case of gross dispersions produced by mechanical techniques. The evidence for this lies in parallel-plate viscosity data, which indicate only a slight difference in viscosity between portions of the samples exposed to current flow and parts not so treated. In fact, the exposed portion had a slightly lower viscosity than the other portion. Previous data had demonstrated that larger agglomerates resulted in increased viscosity in contrast to the situation under discussion.

Additional drift determinations were performed on another pair of similar samples at 65° C. The results of this experiment are shown in Figure 6. At 65° C and constant application of electrical potential, the drift from 10^{14} to 10^8 ohm-cm. is much more rapid, taking place in about 140 minutes. The speci-

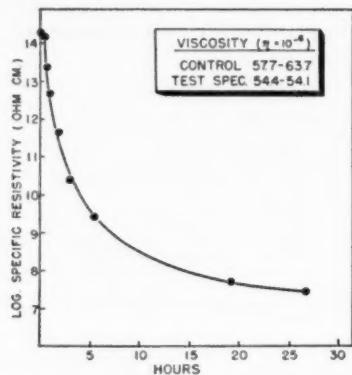


FIG. 5.—Drift in resistivity of an unvulcanized SRF-Butyl system. Under constant electrical potential at room temperature.

mens used were calendered to a gage of 0.075 to 0.080 inch at 300° F. Processing at high temperatures apparently disturbs the particle configuration to a lesser extent than the shearing forces involved when such systems are forced to

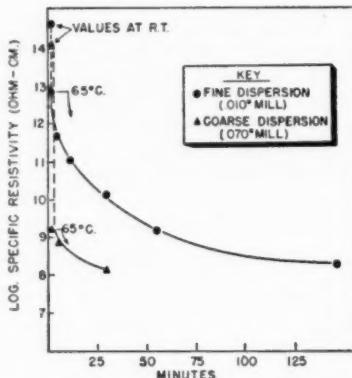


FIG. 6.—Drift in resistivity of unvulcanized Butyl-SRF systems. Under constant electrical potential at 65° C.

flow slowly at low temperatures and high pressures. The resistivity changes before this experiment are indicated in Table IV.

The high resistivity obtained in the gross dispersion, on standing at room temperature, is quite transient at elevated temperature. While both samples showed a lower initial resistivity at 65° C, than at room temperature, the coarse

dispersion showed a much greater drop than the fine dispersion. As a matter of fact, both systems approach their original unaged resistivity value.

This change, however, is reversible. In a final experiment on the same specimens after they had rested approximately 4 months, both fine and coarse dispersions were found to approach a value around 3.0×10^{12} ohm-cm. specific resistivity.

Two distinct types of resistivity drift have now been described qualitatively. An unvulcanized Butyl rubber-furnace black system when allowed to rest, without mechanical, thermal, or electrical disturbances, will tend to approach an equilibrium resistivity value of $\sim 10^{14}$ ohm-cm. This is true even if the specimen has initially a low resistivity, $\sim 10^8$, by virtue of gross dispersion. On the other hand, when such systems of high resistivity are exposed to a continuous flow of direct current, they tend to drift in the opposite direction. This drift is temperature dependent, but in any case the system approaches a minimum value of $\sim 10^8$ ohm-cm.

Both of these effects are somewhat transient. In the case of a gross dispersion which attains high resistivity on aging under static conditions, it has been found that this high resistivity can be dissipated simply by raising the temperature. On the other hand, the low resistivity obtained in such systems

TABLE IV
RESISTIVITY CHANGES DURING AGING AT ROOM TEMPERATURE

Aging time	Resistivity changes (ohm-cm.)	
	0.010-inch mill setting	0.070-inch mill setting
Original, no aging	3.5×10^{14}	1.1×10^9
2 day	3.0×10^{14}	7.9×10^{10}
1 week	4.3×10^{13}	1.6×10^{11}
1 month	6.5×10^{14}	1.2×10^{13}

by electrical forces is reversed on standing under static conditions. Although the reproducibility of the resistivity data is a measure of the precision of these measurements, this exploratory work was intended to be primarily qualitative rather than quantitative in nature. It is visualized that in future work quantitative determinations would be useful. In this connection, knowledge of experimental variables effecting such measurements acquired in the present work will be particularly valuable.

VULCANIZATION STUDIES

These observations led to a study of resistivity changes occurring during, or as a result of, vulcanization. The effects obtained were studied in two systems—mixtures containing vulcanizing ingredients and those with no vulcanizing agents. Fine and coarse furnace black dispersions were prepared in each group, and all compounds were molded both at room temperature and at vulcanizing temperature. The basic formulation was polymer, 100; SRF black, 50; zinc oxide, 5; tetramethylthiuram disulfide, 1; and sulfur, 2 parts. The last three ingredients were added only in the case of vulcanizing combinations. In such cases a large masterbatch containing these curatives in Butyl was made. The carbon black was then added to this masterbatch under carefully controlled conditions. In this way complete formulations were prepared without disturbing the particular pigment dispersions being evaluated. The data obtained in

this study were shown in Table V. The outstanding fact regarding vulcanizing compositions is that the mere presence of sulfur, zinc oxide, and accelerators is not sufficient to alter the resistivity of the systems. Samples prepared at room temperatures, and hence not vulcanized, had the same resistivity as both fine and gross dispersions containing no curatives. However, when molded for 10 minutes at 320° F, the resistivity dropped to a normal value of $\sim 10^7$ to 10^8 ohm-cm. It is worth noting that in this experiment the gross dispersion exhibited less change than the fine one. It is further evident that there was a slight but definite difference in resistivity caused by varying the molding pressure. The latter observation is consistent with data reported by Bulgins⁶.

In the case of nonvulcanizing systems the data are of comparable significance. Samples prepared at room temperature, had as expected, high resistiv-

TABLE V
RESISTIVITY CHANGES DURING VULCANIZATION OF BUTYL-SRF SYSTEMS

Molding conditions	Resistivity change	
	0.010-inch compd.	0.070-inch compd.
Compounds Containing Vulcanizing Agents		
10 min. at 320° F, 200 lb./sq. in.		
10 min. at 320° F, 2000 lb./sq. in.	2.8×10^7	2.9×10^8
2 hr. at room temp., at low pressure	3.8×10^7	4.9×10^8
2 hr. at room temp., at low pressure, aged 1 day	$> 10^{14}$	8.2×10^{10}
	1.5×10^{13}	1.0×10^9
Compounds without Vulcanizing Agents		
10 min. at 320° F, original	5.0×10^{11}	2.6×10^{10}
10 min. at 320° F, aged 2 days	3.1×10^{10}	7.6×10^9
10 min. at 320° F, aged 4 weeks	3.4×10^{10}	2.2×10^{10}
2 hr. at room temp., 20,000 lb./sq. in.	5.5×10^{13}	1.2×10^{11}
2 hr. at room temp., 20,000 lb./sq. in., aged 1 day	$> 10^{15}$	2.6×10^{12}
Sheets Calendered at 300° F, Aged at 65° F, No Pressure ^a		
Original	1.5×10^{14}	4.5×10^9
16 hr. at 65° C	8.9×10^{11}	7.6×10^9
110 hr. at 65° C	3.1×10^{10}	1.2×10^{10}
Same specimen after resting 4 months at room temp.	1.6×10^9	5.7×10^9

^a No vulcanizing agents present.

ity. In the case of the gross dispersion the value is higher than usual, probably because of the effect of molding under high pressure as suggested previously. It is especially noteworthy that these nonvulcanizing systems, even when exposed to curing conditions 10 minutes at 320° F do not undergo the large decrease in resistivity recorded in vulcanizates. The value obtained is $\sim 10^{10}$ ohm-cm., regardless of dispersion. Furthermore, this value is essentially the same as that obtained upon prolonged exposure to the milder temperature of 65° C. The 10^{10} value obtained is apparently stable, as evidenced by tests made on heat treated specimens after standing at rest for four months.

These data seem to indicate that vulcanizing agents alone do not increase the conductivity of polymer-SRF systems. Neither does thermal treatment in the absence of curatives have the effect of true vulcanization on resistivity. Apparently, the maximum resistivity changes are brought about only by actual

vulcanization. This is a remarkable conclusion, which suggests some form of polymer-sulfur-carbon black interaction. Before attempting any theoretical explanation of these phenomena, however, it will be useful to consider some additional experiments.

PLASTOMETRIC STUDIES

The effect on carbon black dispersion of variations in the amount of physical work done on such systems has been described. The measurement of rheological and electrical properties has been discussed and some suggestion made of changes occurring in pigment-particle configuration during vulcanization. It is, therefore, of interest to measure the changes in viscosity or flow properties of Butyl-furnace black systems under such conditions. Investigation of this problem was carried out on the same five samples which were discussed briefly (Figure 1 and Table 1) and in more detail in an earlier paper¹. Inasmuch as these compounds contained no vulcanizing agents, it was possible to measure the viscosity changes incurred by exposure to high temperature and pressure. These differences are shown in Table VI. The viscosity test-specimens were exposed to high temperatures (10 minutes at 320° F) in a laboratory press in small rings, 1 inch inside diameter by 0.150 inch usually employed in preforming

TABLE VI
EFFECT OF VULCANIZING CONDITIONS ON VISCOSITY
OF CARBON BLACK DISPERSIONS

50 parts SRF in GR-I-15

Mill setting (inch)	0.010	0.020	0.035	0.050	0.070
Original viscosity ($\times 10^{-6}$ poises)	39.6	47.9	54.6	51.3	69.2
Viscosity (after 10 min. at 320° F)	36.1	34.4	36.9	45.1	43.9
Difference (ave. of 4 determinations)	3.5	13.5	17.7	6.2	25.3

the test-specimens for the parallel-plate plastometer. The data indicate that the large differences in viscosity existing in the original compounds are minimized by exposure to vulcanizing conditions in this manner. In most instances the magnitude of viscosity change is directly related to the degree of agglomeration: the coarser dispersions showed the greatest loss in viscosity. The one exception is in the case of the mix prepared on the 0.050-inch gage mill. It is not easy to explain this discrepancy. However, in the earlier paper¹ it was pointed out that this compound differed from the others in that the mill bank constituted a substantially greater proportion of this composition than any of the others. It is possible that this results in a more thorough blending of the compound and possibly the agglomerates were more tightly held in the polymer mass than was the case with the other compounds. If this were true, it is at least conceivable that these agglomerates were less readily fractured during the hot molding operation.

Nevertheless, it may be concluded that the effect of heat and pressure on such systems is to minimize existing differences in carbon black dispersions. These changes, unlike electrical drifts, are more permanent and essentially irreversible. This explains why dispersion differences which may give serious processing difficulties in production cannot be readily detected by means of laboratory tests based on the vulcanizate properties of such systems.

VULCANIZATE PROPERTIES

It cannot be stated positively, however, that there are not some subtle differences in the physical properties of these vulcanizates. These properties have been measured in several different ways. In all cases a polymer masterbatch containing all vulcanizing ingredients was used in preparing compounds with varying degrees of SRF black dispersion. Test-specimens were prepared by vulcanizing the samples simultaneously in the same multicavity molds. Stress-strain curves (Figure 7) were obtained on compounds vulcanized for 10 minutes at 320° F. At low elongations the coarse dispersion has a distinctly higher modulus than the fine one, while the latter has a greater ultimate tensile strength of 260 pounds per square inch, an improvement of almost 16 per cent. Tests with the Taber abrader indicate that a definitely higher rate of abrasion loss may be expected with coarse dispersions than with fine ones. After 1000 cycles, the better dispersion had an 0.142 per cent abrasion loss as compared with 0.170 per cent of the coarse dispersion.

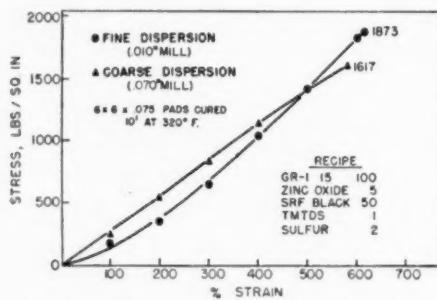


FIG. 7.—Effect of dispersion on tensile properties.

These data support the belief that large agglomerates of furnace black occurring in gross dispersions persist to some extent during the vulcanization process. The higher modulus occurring in such products may be attributed to the viscous effects of the large agglomerates. The superior reinforcing properties of fine dispersions are, however, reflected in higher ultimate tensile strength and better abrasion resistance. Also characteristic of true reinforcement is the lag in modulus at low extensions followed by higher values as orientation effects are induced at increased strains.

SUMMARY AND DISCUSSION

Several facts have been established as a result of this work. The degree of carbon black dispersion or, to be more specific, the degree of disaggregation obtained in SRF black distributed in Butyl rubber, is influenced to a significant extent by the amount of mechanical work done on such mixtures. These differences have been observed repeatedly by means of the electron microscope and photometric and rheological tests. The electrical properties of SRF-Butyl systems are quite sensitive to the conditions to which they are exposed. Changes in electrical resistivity are brought about by variations in temperature or pressure as well as by electrical forces. Most of such changes, however, are reversible, except in the case of vulcanizates. The vulcanization reaction has

an important influence on the electrical properties of such systems. Although the process of vulcanization tends to minimize the differences in SRF pigment dispersion, there is considerable evidence that such differences may persist in vulcanizates and have an important effect on their physical properties.

In view of all these facts one may speculate upon possible explanations for the observed phenomena. Several authors⁷ have, indeed, pointed out that increased shearing action on polymer-pigment systems, obtained by more severe milling conditions, does bring about gross differences in "dispersion." There has always been, however, a need for more precise techniques of measuring and evaluating these differences. It is hoped that the several procedures discussed in this paper will prove to be useful in such applications.

In the present work the polymer-pigment habit in Butyl rubber-SRF systems has been described by these methods. However, the theoretical explanation for some of the phenomena, such as photometric or electrical drifts, is not immediately obvious. Bulgin⁶ and Parkinson and Blanchard⁴ have considered the possibility of changes in carbon structure under various condi-

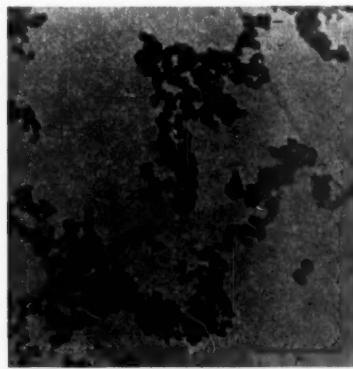


FIG. 8.—Electron micrograph of SRF black.

tions, such as Brownian movement. In the present work it has been shown that photometric and electrical resistivity changes are not accompanied by a comparable alteration in rheological properties. How then may these concomitant but not complementary effects be explained? By what mechanism may such changes occur? A hypothetical case is illustrated in Figure 8, in which some liberties have been taken with an electron micrograph of SRF black. Here the formation of continuous chains for passage of a current in the presence of an electrical field is proposed. Such a mechanism is suggested by work of Cohan and Watson⁸, Voet and Suriani⁹, and Pohl¹⁰. Under the influence of an electrical field dipoles may be induced on suspended particles. The particles can then coalesce into conductive chains throughout the rubber matrix. They do this more readily when the temperature is raised and the viscosity of the rubber matrix is reduced. This electrical drift in unvulcanized systems is reversible, for the compounds in Figure 6 returned to their original values on standing a few weeks. Furthermore there appears to be no good reason why formation of conductive chains by a mechanism involving induced dipoles could

not take place without fracture of existing agglomerates. This view is indeed consistent with the present data.

It has already been suggested that the changes in light transmittance values are related to the formation of bound Butyl. Here, too, it seems reasonable to expect that some portions of carbon aggregates can form an association with the polymer without actually breaking up the agglomerate structure. Thus, bound rubber formation could proceed without altering the rheological properties appreciably. The initial drop in light transmittance value in the case of very coarse dispersions might be explained by the hypothesis that the swelling of the polymer in solution does actually cause fracture of very large agglomerates.

There is, indeed, some theoretical evidence to support the concept of carbon black-polymer interaction of a type that could produce bound rubber. Naunton and Waring¹¹, Gehman and Field¹², and Thornhill and Smith¹³ have suggested that strong bonds exist between polymer and pigment and that these bonds may be related to unsaturation. In reviewing work in this field, Parkinson¹⁴ proposed the existence of primary valence linkages between carbon pigment and polymers. This concept has been advanced more recently by the work of Stearns and Johnson¹⁵. It should perhaps be pointed out that these concepts must be approached with some caution. The distinctions between primary valence linkages, van der Waals forces, and physical associations are difficult if not impossible to detect in such systems as the ones under discussion. It is reasonable to assume, however, that some such forces are involved in bound rubber as well as reinforcing phenomena.

It was suggested earlier that an interaction between carbon black and the cross-linking polymer occurs during vulcanization with sulfur. This thought was based on several observations made on the electrical properties of vulcanized and unvulcanized systems. It was found that the presence of sulfur and other curatives in mere physical admixture in a polymer-black system has no effect on the electrical resistivity. Likewise, the application of vulcanizing temperatures, in the absence of vulcanizing agents, does not bring about the degree of change promoted by actual vulcanization.

In speculating on the reasons for this behavior, it is convenient to accept certain concepts which have been reasonably well established. Vulcanization is believed to be a series of complex chemical reactions in which strong intermolecular forces are formed between rubber molecules¹⁶. These changes are thought to involve reactions with the alpha-methylene carbon atoms or double bonds, with a possible reduction of polymer unsaturation. These chemical bonds between rubber molecules account for the conversion of the soft plastic unvulcanized rubber into a tough elastic infusible and insoluble vulcanizate. The magnitude of the permanent change in resistivity on actual vulcanization suggests some form of interaction between polymer, pigment, and curatives. Some observers have proposed that this is simply a matter of flocculation, but this idea does not seem to fit all the experimental observations. Another possibility is that this is a viscosity effect. Viscosity being temperature dependent, a lower resistivity is obtained at vulcanizing temperatures, the particular pigment configuration responsible for low resistivity becoming permanent on vulcanization. It is true that resistivity does decrease rapidly during vulcanization. That this change is permanent and irreversible can undoubtedly be attributed to the fact that a rigid polymer network is formed which does not permit any easy change in pigment particle configuration.

However, still another hypothesis is suggested by the present work. There appears to be a possibility that the strong polymer cross-linking forces created by vulcanization disrupt weaker polymer-pigment bonds. In this way the pigment particles are forced into more conductive chains. This concept presents an interesting possibility—if some method of strengthening polymer-pigment bonds can be devised, a true enhancement in polymer reinforcement may be realized.

It is acknowledged that some of the points made and conclusions suggested in this paper are of a controversial nature. This is unavoidable and even desirable in a field where further investigations are needed. It is hoped that these circumstances will stimulate additional investigations, particularly where further elucidation would contribute to a better understanding of reinforcing phenomena. Studies of other types of pigments as well as all carbon black types would seem especially worthwhile at this time. The practical value of some of these findings should be obvious. Their application to specific problems in the fabrication of inner tubes, coated fabrics, insulated wire, and similar products is suggested.

SUMMARY

Previous studies have shown that differences in milling conditions cause significant variations in the dispersion of SRF black in Butyl rubber. Recent work has placed such differences on a more quantitative basis. This was achieved by the interrelation of photometric, rheological, and electrical measurements. These observations revealed new phenomena involving changes in the pigment-polymer habit of such systems. Analysis of these phenomena has led to the conclusion that they may be interpreted as evidences of pigment-polymer association.

ACKNOWLEDGMENT

The authors are indebted to A. Y. Mottlau for the electron micrographs and to D. L. Crow for the illustrations and graphs. Most of the laboratory experiments were performed by F. J. Blash. The writers received valuable assistance and suggestions from many other associates during the course of the work and in preparation of the manuscript.

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ACTION OF LIGHT ON SODIUM-BUTADIENE RUBBER *

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Light aging is one of the basic causes of the destruction of rubber and rubber products. In view of this, it seemed interesting to study the structural changes which take place in rubber under the influence of light. It is known that light not only activates the oxidation process, but also has another quite independent effect on rubber. When exposed to light, sheets of rubber (sodium-butadiene-polymer and natural rubber) lose their capacity to form solutions, and already prepared concentrated solutions (up to 10 per cent) form gels.

The work of Zhukov, Komarov, and Sibiryakov¹ showed that, when benzene solutions of purified sodium-butadiene rubber are irradiated, the viscosity of the solution drops under the influence of the light, and gelation then takes place.

In a work on the irradiation of solutions of natural rubber with a mercury-vapor quartz lamp, Soboleva² showed that, in the first stages of irradiation, a decrease of molecular weight is observed, and then an increase at more advanced stages. From this the author concludes that, as a result of the action of light, there is not only a destructive reaction, but also a reaction leading to structural formation. The quantum yield of these processes is very small (approximately $4 - 12 \times 10^{-4}$); on the basis of this, Soboleva offers the suggestion that the process is not a chain process.

Bateman³, studying the photolysis of carefully purified natural rubber in a vacuum, observed a breakdown of the rubber hydrocarbon and liberation of gaseous products containing 70 per cent hydrogen. This led the author to the conclusion that rupture of the carbon-hydrogen bond takes place in distinction to thermal decomposition, whereby the carbon chain is shattered. As Bateman remarks, however, the formation of gaseous products is only one characteristic of primary dissociation. An approximate calculation of the quantum yield (with falling energy) of the gaseous products formed is 4×10^{-4} .

It should be noted that the most serious failure of nearly all investigations of the effects of light on rubber is that no consideration has been taken of the reactions leading to the complex structural changes which take place in polymers. Another essential failure is that the authors calculated the energy of the impinging light but not the energy absorbed in the reactions responsible for the changes in the polymer.

EXPERIMENTAL METHOD

A study of structural changes taking place in a sodium-butadiene polymer (hereafter the sodium-butadiene polymer will be called "the polymer") under the influence of light was made in a high vacuum at 25° C. The polymer was carefully purified from extraneous substances by double precipitation from

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benzene solution by methanol, and then was brought to a constant weight in a vacuum. Sheets of standard dimensions were formed on the surface of the water. Frames for the sheets were 35 \times 65 mm. in area and 50, 100, and 200 microns thick. The benzene and water absorbed by the sheet of polymer were removed in a vacuum. All the operations of purifying the polymer and making sheets of it were carried out in a special apparatus which excluded all leakage of atmospheric oxygen.

The degree of unsaturation according to Vasilyev⁴ was 92 per cent of the theoretical value. The number of double bonds in the main chain, determined by the perbenzoic acid method, was 32 per cent of the total amount.

The relative viscosity of the 0.3 per cent benzene solution was 1.8, measured with an Ostwald viscometer. A general scheme of the experimental apparatus used in the study of light aging of polymer sheets is shown in Figure 1.

A sheet of polymer was inserted in a glass frame, and this was placed in the quartz vessel 1. The vessel (of diameter 48 mm., and height 210 mm.) was

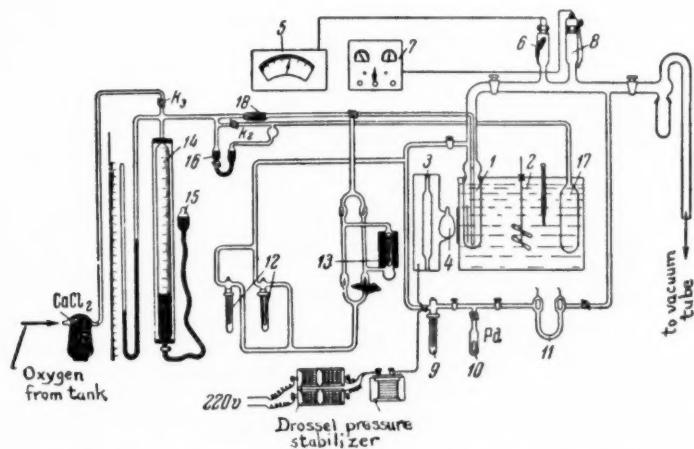


Fig. 1.—Diagram of experimental apparatus for study of the light-aging of rubber.

placed in a liquid thermostat 2 and contact thermometer. A mercury-vapor quartz lamp in a water jacket was used for the source of irradiation. The light energy emitted by the lamp was concentrated on the surface of the sheet by a round quartz retort 4, filled with distilled water. The pressure in the system, from 10^{-1} to 10^{-6} mm. of mercury, was measured with a vacumeter 5 and lamp 6. For measuring small pressures from 10^{-4} to 10^{-6} , an ionization vacumeter 7, and an ionization lamp were used.

For trapping the condensing portions (at 180° C) of gaseous products of decomposition of the polymer, a trap 9, cooled by liquid nitrogen, was used. For detecting hydrogen from the portion of gaseous decomposition products of the polymer which did not condense at 180° C, a trap 10 of palladium-tin was used. For determining quantitatively the hydrogen content, a discharge tube 11 with aluminum electrodes was used. The system was pumped for 25-30 hours at room temperature with traps cooled by liquid nitrogen; after this the gas yield of the sheets was determined. Sheets were considered degassed if,

after two hours, no change of pressure was observed in the system. The degassed sheet was exposed to radiation and, at the same time, the amount of volatile products in the gaseous phase was measured.

EXPERIMENTAL RESULTS

VOLATILE PRODUCTS OF THE REACTION

Figure 2 shows the results for the yield, in a vacuum, of volatile products in the process of irradiating sheets of polymer of varying thickness. The figures which are shown are the arithmetic average of 4 or 5 measurements, and the deviation of individual measurements from the average value was 1-2 per cent. The quantity of gaseous byproducts is expressed in gram-moles per mole of polymer. The calculation of the volatile substances is based on a structural unit (mole) of the original polymer containing one aliphatic double bond. For sodium-butadiene rubber, the mole is 54 grams.

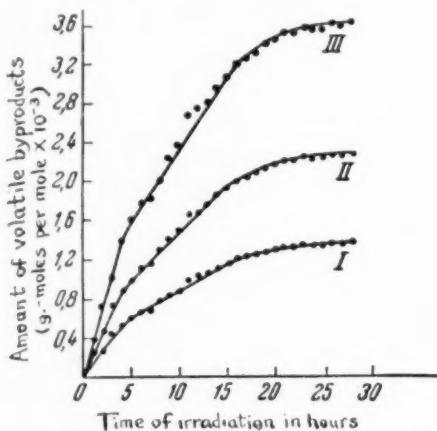


FIG. 2.—Kinetics of yield of gaseous products during irradiation of sheets of polymer of varying thickness in vacuum. I, thickness of sheet 200 μ ; II, thickness of sheet 100 μ ; and III, thickness of sheet 50 μ .

Figure 2 shows curves describing the process of production of gaseous by-products during irradiation of sheets of varying thickness (I, 200 μ ; II, 100 μ ; and III, 50 μ). Characteristic of these curves is the presence of a deflection in the initial stage of radiation at 4 hours. Thereafter the rate of gas formation remains constant for a protracted period, and finally begins to fall after a long time of irradiation.

Presumably this bend in the curve is related to the unequal distribution of radiating energy, which in the early stage of the process is mostly absorbed by the outer surface of the sheet. Then, in proportion to the extension of the process into the lower layers of the sheet, a decrease of speed of reaction is observed. The correctness of this assumption is confirmed by experiments with sheets of varying thickness.

Thus, curves I, II, and III show that the relative quantity of gaseous products formed during the irradiation decreases with increase of thickness of the sheet.

The increase of pressure observed in the system is the result of the formation of volatile byproducts, and is not explainable by experimental errors (low precision of measurements, effect of oxygen, etc.). This assertion is based on the following special experiments performed by the authors with a sheet of thickness 100μ (see Figure 3, curve 1):

1. At a certain point during the process (10 hours), the radiation was shut off and, after evacuation of the system, the sheet was again irradiated for 40 hours. Figure 3 (curve 2) shows that complete kinetic reproducibility of the system takes place.

2. At a certain point during the reaction (8 hours), a small quantity of oxygen was added to the reaction vessel, and then radiation was continued for 7 hours. The experimental results in Figure 3 (curve 3) show that, after the admission of oxygen, the rate of evolution of volatile byproducts remained constant.

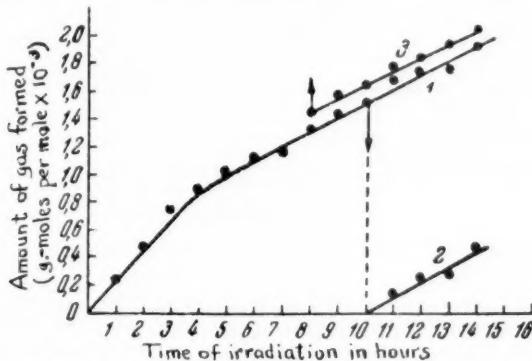


FIG. 3.—Kinetics of yield of volatile byproducts during irradiation of sheet of polymer in vacuum (thickness 100μ).

Thus the yield of volatile byproducts observed during radiation is a result of partial decomposition of the molecules in the polymer; this is confirmed by direct analysis of the volatile products. Thus the gaseous part was found to consist of 32 per cent methane and 62 per cent hydrogen. The composition of the volatile byproducts is determined by fractional combustion on copper oxide in a Lung apparatus.

DETERMINATION OF THE QUANTUM YIELD OF VOLATILE BYPRODUCTS

The amount of energy absorbed by a sheet was measured by analysis of a solution of oxalic acid placed in a quartz cuvette. The cuvette was placed in the reaction vessel behind the sheet. The concentration of oxalic acid was 0.05 mole per liter. The amount of volatile byproducts was 2.46×10^{-4} gram-mole per mole of polymer. The quantum absorbed by a mole of polymer was $1.26 \times 10^{-1} N$, where N is the Avogadro number. The quantum yield was 2×10^{-3} .

STUDY OF STRUCTURAL CHANGES IN A POLYMER

Study of a sheet polymer after irradiation showed that essential structural changes had taken place internally.

1. The solubility decreased, as is seen in Figure 4.
2. The degree of unsaturation decreased, as can be seen in Figure 5. The quantum yield according to the change of unsaturation was 0.73. This value for the quantum yield appears low because the calculations were made with the assumption that all of the energy absorbed by the rubber causes changes in the polymer.

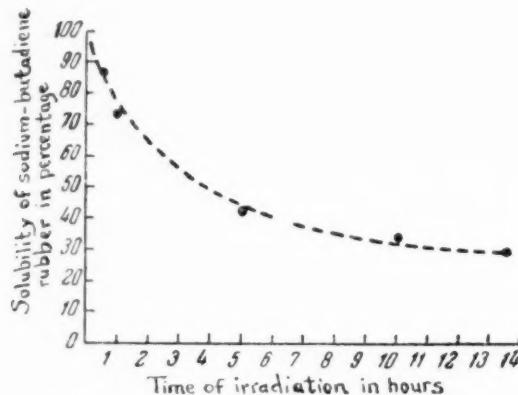


FIG. 4.—Change of solubility of polymer as a function of the time of irradiation in a vacuum.

3. Infrared spectroscopy revealed that, during irradiation, the number of double bonds located in the main chain decreases much faster than the number of double bonds in a side chain. For example, after the first hour of irradiation, the decrease of double bonds in the main chain was 25 per cent, whereas the decrease of double bonds in a side chain was only 3 per cent. After 13.5 hours

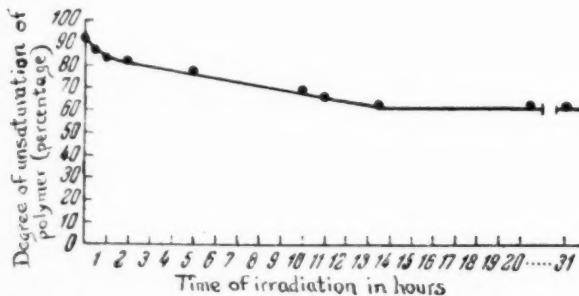


FIG. 5.—Change of unsaturation of polymer as a function of the time of irradiation in a vacuum.

of irradiation, no double bonds were present in the main chain of the polymer, and in a side chain only 6 per cent remained.

The proportion of double bonds in a side chain of the original polymer was 68 per cent, and in the main chain 32 per cent.

These data show that, during irradiation in a vacuum, complex reactions

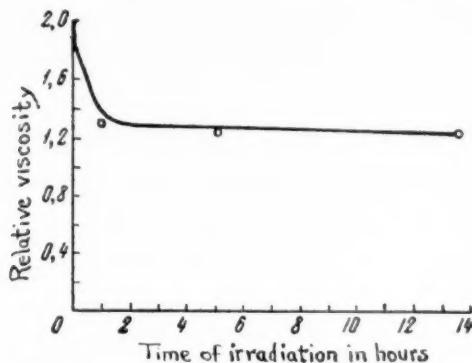


FIG. 6.—Change of relative viscosity of the sol fraction of polymer in relation to time of irradiation.

take place in a polymer, and that they are related in some way to the formation and subsequent transformation of radicals.

4. The relative viscosity of the sol fraction (see Figure 6) changes rapidly during the first hour of irradiation, after which hardly any changes are observed. Presumably the decrease of viscosity is related to the gradual enrichment of the sol fraction of the polymer by low-molecular fractions.

CONCLUSIONS

An apparatus was devised and experimental methods of investigating the action of light on polymers in a high vacuum (10^{-6} mm. of mercury) were developed. The limits of accuracy of the methods for measuring gas formation and decrease of unsaturation are 1–2 per cent.

The effect of ultraviolet radiation on sodium-butadiene rubber in a high vacuum is the formation of gaseous byproducts. The latter appear as two fractions: one which condenses at 180°C , and one which does not condense under the same conditions. The noncondensing part comprised 84 per cent of the total, and consisted of 64 per cent hydrogen and 32 per cent methane; this indicates rupture of the $-\text{C}-\text{C}-$ and $-\text{C}-\text{H}$ bonds.

The action of light on rubber is accompanied by a loss of unsaturation. The change of unsaturation is primarily in the main chains and only to a small degree in the side chains (we know that the reverse is true with respect to the effect of heat).

Measurements were made of the light energy absorbed by rubber, and the quantum yield of gaseous products was calculated. The small quantum yield (2×10^{-3}) indicates the incatenate nature of the process.

The decrease of solubility of an irradiated polymer is a consequence of a reaction between free radicals forming after rupture of the $-\text{C}-\text{H}$ bond, and also after rupture of the carbon chain.

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CRACKING OF RUBBER AND GR-S IN OZONE

EFFECTS OF TEMPERATURE AND ELONGATION *

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For several classes of rubber articles, the presence of cracks caused by ozone may be considered primarily an appearance defect, because the cracks do not interfere with the performance of the product. The subjective severity of cracking is determined solely by the size and number of cracks and it is interesting to consider how the size and number of cracks are influenced by the service environment of the articles. Experience had led to the belief that temperature is one of the more important environmental factors influencing cracking appearance, so a study was begun to determine some of the effects of temperature on ozone cracking.

PREVIOUS WORK

The effects of temperature and elongation on the appearance of cracks produced in natural rubber by ozone have been reported by various writers. Williams¹, Shephard², and others demonstrated that the crack density, *i.e.*, the number of cracks per unit area, in samples of rubber exposed to ozone at constant temperature increased with increasing elongation. The relation between crack density and temperature was reported by Crabtree and Kemp³ and Kearsley⁴, who found that increasing the temperature had the same effect as increasing the elongation. In addition, Kearsley reported that samples which were kept frozen during exposure did not crack.

The combined effects of temperature and elongation on cracking were reported by Ball, Youmans, and Rausell⁵, who, in studying two natural-rubber compounds at a series of elongations and temperatures, found that the severity of cracking reached a maximum for all elongations at about 25° C, decreasing in severity above and below this temperature. This result was interpreted by them as indicating that the critical stress was as important as the critical elongation, since their data showed that the moduli of the two compounds were very nearly the same in the region of maximum severity of cracking. Although this would seem to be inconsistent with the previous work, the conclusions become entirely consistent if the observations of the dimensions of the cracks are translated into terms of crack density.

To summarize, both temperature and elongation have been found to have similar effects on the crack density of natural rubber samples exposed to ozone. This may be interpreted as indicating that the stress in the sample is the factor which determines the crack density, since stress in elastomers is a function of elongation and temperature. Support for this view is given by the fact that, independent of temperature, elongated samples which exhibit rapid stress

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TABLE I
EXPERIMENTAL RECIPES

	Rubber	GR-S	Low-temperature GR-S
Smoked sheet rubber (No. 1)	100	100	
Standard GR-S			
GR-S X583			100
MPC black	40	40	40
Hydrocarbon oil		6	6
Pine tar	4		
F. C. zinc oxide	5	5	5
Stearic acid	3	1	1
MBT ^a	0.75	1	1
DPG ^b		0.20	0.80
Sulfur	3	2	2

^a Mercaptobenzothiazole.

^b Diphenylguanidine.

decay either fail to crack or show smaller crack densities when allowed to stand for a time prior to exposure to ozone.

The data presented by Ball do not agree with this interpretation, as they show that both the resistance to cracking and the modulus increase with decreasing temperature; unfortunately, complete modulus data were not given for elongations lower than 50 per cent, but it is presumed that the same behavior would be shown at the lower elongations. These data are not anomalous, but actually represent the stress-temperature behavior of rubber under nonequilibrium conditions of stress, and it is necessary to seek for another explanation of the effect of temperature on crack density.

In the present work Ball's studies were extended to a standard GR-S and a low-temperature GR-S compound with the hope of clarifying the relationship between elongation, temperature, and ozone crack density. The two types of GR-S differ in their temperature behavior sufficiently from rubber to be of interest in this type of study. A rubber compound was included as a control.

EXPERIMENTAL

The recipes of the compounds which were studied are shown in Table I, and some of the physical properties of these compounds are shown in Table II.

These compounds are similar to those used in tire treads or sidewalls but were deliberately simplified. Antioxidant was omitted to avoid complications which result from differing activities in the polymers. One-inch wide strips of these compounds were cut from $4 \times 6 \times 0.08$ -inch tensile slabs which had been cured for 45 minutes at 292° F. These strips were clamped in a rack of the type shown in Figure 1 and stretched to the desired elongation at room tem-

TABLE II
ROOM TEMPERATURE PROPERTIES OF EXPERIMENTAL COMPOUNDS^a

	Rubber	GR-S	Low-temperature GR-S
Tensile strength (lb./sq. in.)	4400	2180	2300
100% modulus (lb./sq. in.)	230	170	180
Breaking elongation (%)	640	593	493

^a Cured 45 minutes at 292° F.

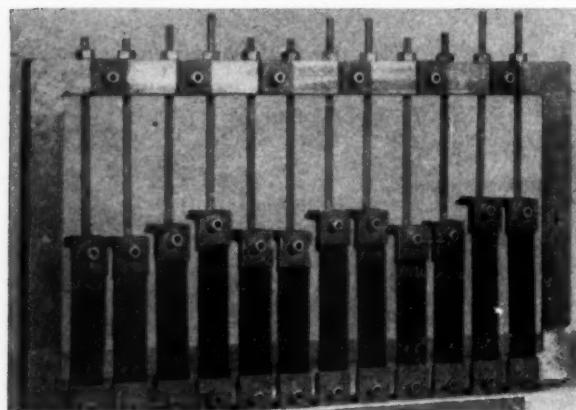


FIG. 1.—Testing rack.

perature. The stretched samples were then placed in an ozone chamber (Figure 2) employing a voltage-regulated silent discharge ozone generator with a thermostatically controlled heater-blower and refrigerating system, and a carefully regulated air flow. The samples were allowed to stand at the testing temperature for at least 1 hour before the ozone generator was started in order to reach thermal and mechanical equilibrium. They were then exposed to a concentration of ozone of 1.4 ± 0.1 p.p.m. for 4 hours at temperatures ranging from -10° to 90° F; the maximum temperature variation during a run was $\pm 2^{\circ}$ F. Sample relaxation during conditioning was not measured directly, however the relative equilibrium stress in the synthetic compounds is shown in Table III.

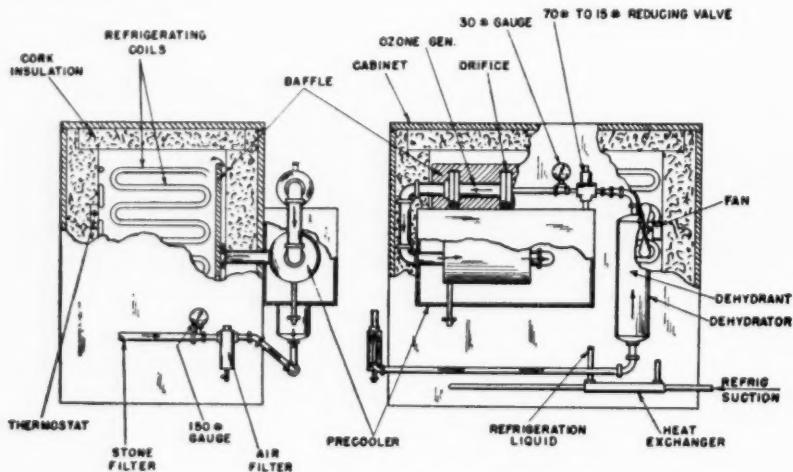


FIG. 2.—Ozone test chamber

The ozone concentration in the box at the time of exposure was determined with an apparatus of the type described by Crabtree and Kemp³, in which the stream of ozonized air passes through a fine spray of buffered potassium iodide solution, thereby ensuring rather complete contact of the ozone with the solution.

TABLE III
RELATIVE STRESS AS A FUNCTION OF TEMPERATURE AND ELONGATION

Temp. (° F.)	Elongation (%)	Relative stress	
		Standard GR-S	Low-temperature GR-S
90	10	4.64	6.37
	15	5.47	7.48
	20	5.98	7.91
50	10	5.62	7.26
	15	6.55	7.67
	20	6.30	8.09

tion. Results obtained by this method of analysis are claimed by the designers to be not affected by small amounts of nitrogen dioxide or other oxides of nitrogen which may be formed in the ozonizer.

RECORDING RESULTS

A simple method was devised for recording the appearance of the cracked samples. The surface of the cracked sample is first wiped with a clean cloth to remove any dust. The sample is then pressed against a stamp pad saturated with an ink such as Carter's stamp pad ink (selected as most suitable after several trials with various inks) and the excess ink is wiped off on the pad. The sample is next placed in a small rack and stretched to open the cracks so

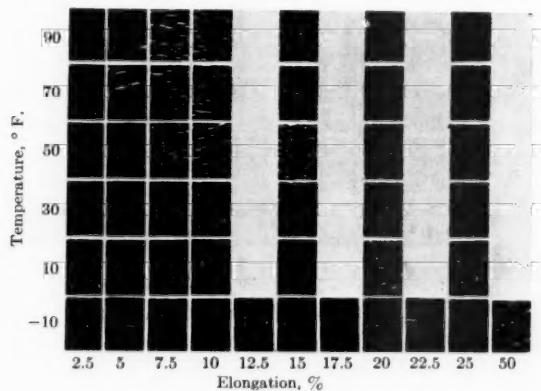


FIG. 3.—Natural rubber.

that a clear impression will be obtained, after which it is placed over a sheet of bond paper, inked side down, and lightly pressed against the paper with a small roller. With a little practice, this method gives a clean print of the sample and shows clearly the number and size of even small cracks.

RESULTS

Figure 3 shows prints of the cracked natural-rubber samples. It is seen that at each temperature, with the exception of the two lower temperatures, the crack density increases with elongation and the crack size decreases with increasing elongation.

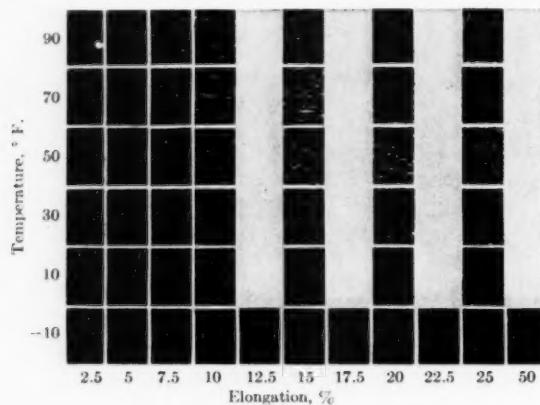


Fig. 4.—Standard GR-S.

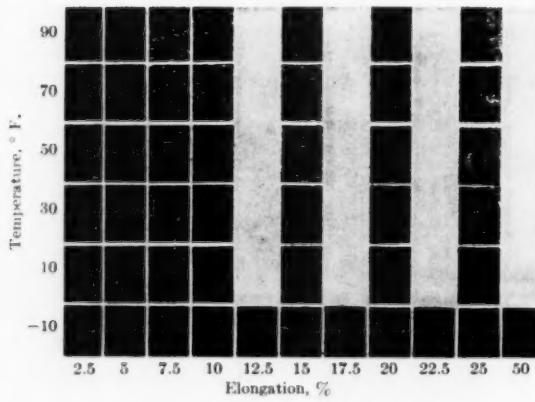


Fig. 5.—Low temperature GR-S.

In Figures 4 and 5 are shown the prints of the standard GR-S and low temperature GR-S compounds. The cracking shown here is qualitatively the same as that produced in the rubber compound.

In each set of prints it is seen that for each temperature there is an elongation below which no cracking occurs; this elongation has been termed the *cracking threshold*. Although the exact determination of the cracking threshold presents some difficulties because of sample nonuniformity, it is possible to determine roughly the relation of this elongation to temperature. In Figure 6

the cracking threshold for the samples shown previously is plotted against the temperature of exposure. The curves are approximately hyperbolic and lie in the same order as the moduli of the compounds.

DISCUSSION

It has been found here that temperature and elongation have similar effects on cracking density and that there is a cracking threshold which is a function of the temperature and which may depend on the modulus of the compound. The relation between cracking threshold and temperature seems to be qualitatively the same for the three types of compounds examined. From this it may be inferred that the three polymers possess a common property which is affected by temperature to produce changes in ozone crack density. It is still desirable to offer some explanation for the similarity of the behavior of these compounds and the shape of the cracking threshold-temperature curves.

The first hypothesis which might be examined is that the stress in the sample determines the crack density. This would mean that the cracking threshold

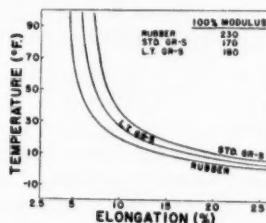


FIG. 6.—Cracking threshold as a function of temperature.

could be interpreted as the minimum stress necessary to crack the sample at a given temperature. This hypothesis is shown to be incorrect, however, by an examination of the relative stresses in the samples at the elongations and temperatures used (Table III). These were determined indirectly by measurement of the resonant frequency of small strips of the samples which were held at constant elongation.

For each compound the relative stress increases with decreasing temperature, in agreement with the work of Ball; therefore, stress cannot be the sole factor in determining crack density, since it is not reasonable to assume that crack density decreases with increasing stress.

A thermodynamic and kinetic consideration of the crack density-temperature relationship may lead to a more productive analysis. During a discussion at the Gordon Research Conference (Colby Jr. College, New London, N. H., July 9-13, 1951) it was proposed that scission of a molecule under strain may be permanent because of the separation of the two radicals at the point of scission, whereas the molecule in the unstrained state may allow recombination of the two radicals formed during scission⁷. This proposal could explain both the temperature and strain relationship of ozone cracking. If free radicals are intermediate products in the ozone rubber reaction, they would have a greater chance of recombining or relinking at a low temperature than at a high temperature; this greater probability of recombining, however, could be overcome by increasing the strain.

Another interpretation of the data is suggested by the fact that the tensile strength of most materials increases with decreasing temperature. If the formation of ozone cracks in elastomers is considered simply as a breaking process, then the stronger the surface ozonide film, the fewer the number of cracks which will be formed at a given stress⁸. Thus, the effects of temperature and elongation on crack density may in this case be interpreted in terms of their effects on the absolute stress, rate of surface stress relaxation, and surface-film tensile strength.

Unfortunately, the quantitative relations of these various factors to crack density are unknown, and the difficulties of developing an exact relationship are manifold. Fortunately, however, use may be made of the concept of the cracking threshold without a quantitative knowledge of its relation to temperature, etc. For certain products, cracking is not objectionable if the cracks are very small and dense. However, the service conditions of the product may involve temperatures or elongations which tend to produce the large, scattered cracks. In this case it is usually possible, through a study of the effects of compounding variables on the cracking threshold, to design a compound in which the cracking will be of a less objectionable type or which will not crack under special service conditions. Work of this type is aided considerably by the examination of prints of samples exposed to ozone at a variety of temperatures.

SUMMARY

Determinations of the effects of elongation on the character of cracking in samples of rubber exposed to ozone have been reported by some of the early workers in the field. Data on some of the effects of temperature on the rate and character of cracking have not clearly shown the effects of the interaction of temperature and elongation on the character of ozone cracking. In the present study, samples of rubber, standard GR-S, and low-temperature GR-S compounds were exposed to a constant concentration of ozone for 4 hours at several elongations and temperatures. Prints were made from the exposed samples by inking the sample surface and taking an impression on paper. The rubber compound cracked at lower temperatures and elongations than either the standard or low-temperature GR-S compounds, and for each temperature there existed an elongation below which no sample cracked; this elongation is termed the *cracking threshold* for this temperature. The cracking threshold was found to be a function of the temperature, decreasing with increasing temperature. Although this relation is particularly difficult to treat exactly, it is possible to explain this effect on the basis of changes in ozonide film strength and ozonide stability with temperature. Studies of the effects of compounding on the cracking threshold may be of great value in designing compounds to fit the climatic conditions where they are to be used.

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STATIC EXPOSURE TESTING OF AUTOMOTIVE COMPOUNDS *

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Deterioration of rubber in service due to cracking is a problem of major concern to all manufacturers and consumers of rubber products. Automotive manufacturers each year face losses aggregating thousands of dollars because of premature cracking and failure of rubber parts. The problem of the rubber technologist is complicated by the fact that ozone cracking of a given compound out of doors is a variable factor, depending on meteorological conditions and geographical location. Cracking also varies with the amount of strain imposed in the automotive assembly. A satisfactory rubber must resist ozone cracking regardless of the locality. This is not easily achieved because of the seasonal variation in ozone concentration in various parts of the country. Ozone ranks with oxygen, heat, light, and oils as a deteriorating agent for vulcanized rubber.

This study shows that there are many variables which must be observed in order to obtain uniformity in weather aging. Because of a variation in ozone concentration from one place to another, outdoor weather-aging results are not necessarily the same. During June and July 1951, 188 duplicate exposure tests were run in Chicago, Ill., and Clearwater and Miami, Fla., on commercial weatherstrips according to SAE-ASTM procedure. Seventy-seven samples (40.95 per cent) gave the same degree of cracking in Chicago and Florida, while 102 samples (54.25 per cent) showed less cracking in Florida than in Chicago. Only 9 samples (4.8 per cent) cracked more in Florida than in Chicago. In winter these conditions may be reversed.

The SAE-ASTM ratings given in Table I show that checking in Chicago was more severe than in Florida under these conditions. Clearwater, Fla., was

TABLE I
CHICAGO VS. FLORIDA EXPOSURE

	Less cracking than in Chicago	Same degree of cracking as in Chicago	More cracking than in Chicago
Clearwater	68	49	6
Miami	34	28	3
Total ^a	102	77	9
Per cent	54.25	40.95	4.8

^a Grand total, 188.

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less severe than Miami, Fla. The number of samples giving a certain rating are given for each location, as follows:

	SAE-ASTM rating			
	0	1	2	3
Chicago, Ill.	—	36	62	26
Clearwater, Fla.	26	59	26	11
Miami, Fla.	6	38	13	6

It was observed that the exposure rating of a given compound varies from day to day. This was due to some uncontrolled variables in materials or handling.

Accelerated tests in an ozone chamber show ozone resistance of rubber, but do not take into account the effect of sunlight, water, etc. Some compounds which show little or no cracking in an ozone chamber do not show good outdoor weathering, and vice versa.

Fifty-four samples were exposed in Chicago, Ill., and Miami, Fla., and also in the ozone chamber for 70 hours at 100° F in 25 parts ozone per 100 million parts of air. Thirty-nine of the samples were also tested in Clearwater, Fla., and in the ozone chamber. Table II shows that, while the accelerated ozone

TABLE II
OZONE CHAMBER VS. OUTDOOR EXPOSURE

	Total tests	Less cracking than in ozone chamber	Same degree of cracking as in ozone chamber	More cracking than in ozone chamber
Clearwater, Fla.	39	26	8	5
Miami, Fla.	54	33	11	10
Chicago, Ill.	54	27	15	12

test is more severe than a 30-day outdoor exposure, over 20 per cent of the tests show more cracking outdoors than in the ozone chamber. It is possible to select compounds on the basis of ozone chamber tests that do not show up well on outdoor exposure.

The following table gives the SAE-ASTM rating of the above samples. The ozone chamber gives more severe cracking than Chicago or either Florida location, as judged by percentage of samples which rated class 2 and 3. The ozone chamber, however, indicates greater ozone resistance than was actually observed in Chicago and Miami. In the column rated 0, only Clearwater gave more samples with a rating of 0 than the ozone chamber.

	Total no. of samples	SAE-ASTM rating				Percentage of samples at various ratings			
		0	1	2	3	0	1	2	3
Chicago, Ill.	54	8	21	13	12	14.8	39.0	24.0	22.2
Clearwater, Fla.	39	12	15	8	4	30.5	38.5	20.5	10.5
Miami, Fla.	54	6	26	17	5	11.0	48.0	31.8	9.2
Naugatuck ozone chamber	54	10	7	21	16	18.4	13.0	39.0	29.6

The SAE-ASTM Technical Committee on Automotive Rubber has developed a standard method of exposure testing which has resulted in better correlation between laboratories and has been a useful tool in the improvement of

the weather aging of rubber products. It is hoped that a laboratory test can be developed which will correlate with outdoor exposure.

The work of Crabtree and Kemp¹, Newton², Williams³, van Rossem and Talen⁴, Fielding⁵, Buist and Welding⁶, and many other investigators has contributed greatly to an understanding of the effect of light and ozone on rubber. Rubber after exposure to weathering may be classified as crazed, cracked, chalked, or frosted, depending on compounding and the conditions of exposure.

Light-energized oxidation produces a crazed appearance, *i.e.*, a network of fine irregular cracks in a hard inelastic skin or resinous layer⁷. This surface skins acts as a barrier to ozone, and cracking is retarded for some time. Exposure to rain leaches out oxidation products, accentuating the crazed appearance. Temperature changes or flexing may crack the resinous layer, after which cracks will form.

Cracking is produced by the action of ozone on stretched rubber. There is enough ozone in the atmosphere to cause cracking, and light is not necessary. Other gases which may be present in the air—oxides of nitrogen, sulfur dioxide, and chlorine—do not produce cracking⁸. Stretched rubber cracks as rapidly at night as in the daytime and very often more rapidly in the shade than in sunlight. Thompson showed that rubber must be stretched before cracking occurs⁸. Unstretched rubber absorbs ozone until a film of ozonide is formed, but no cracks are produced.

Frosting is the end product of an oxidation process produced by ozone⁹. A freshly vulcanized surface may become dull and frosted within a few minutes to several hours because of the formation of many minute cracks.

Chalking occurs during weather aging, particularly on compounds containing a mineral loading. It is due to oxidation of the rubber on the surface, resulting in release of the filler. Chalking occurs late in weathering, while frosting appears early.

Ozone is formed in the stratosphere by the action of ultraviolet light from the sun on the molecules of atmospheric oxygen. Ozone absorbs the greater part of the ultraviolet light from the sun, otherwise life as it exists on earth would be impossible. The ozone content of the stratosphere is equivalent to a layer 3 mm. thick¹⁰.

The daily ozone concentration at the earth's surface varies from 0 to 6 parts per 100,000,000 parts of air by volume. Winds and convection currents bring the ozone to the earth's surface, the concentration usually being higher on windy days¹¹. Heavy rain stabilizes the ozone content by washing gases from the air¹². Foggy or sultry conditions may result in total disappearance of ozone because of failure of winds to renew the supply¹³.

Ozone is a powerful oxidizing gas and destroys bacteria, molds, and odors. This oxidation is accelerated by increase in the relative humidity. It is decomposed by catalysts, water vapor, and many surfaces. Ozone is reduced by organic matter, dust, smoke, nitrogen peroxide, contact with wood, calcium carbonate, sulfur dioxide, and metallic oxides¹².

EXPOSURES IN CALIFORNIA

Failure of weatherstrips in a windshield assembly is illustrated in Figure 1. Such failures occurred at the corners, the point of greatest strain, in less than 90 days in California. Cracking also occurred on the straight section of the weatherstrip, but not so frequently as at the corners. Commercial weatherstrips were exposed for 28 days during December 1949 in Long Beach, Calif.,

on a 2-inch mandrel. Rubber showed severe cracking, while GR-S gave good results. A blend of rubber and GR-S gave good results in one sample, whereas the second sample shows cracking (Figure 2C). Photographs of the rubber, GR-S, and the blend of rubber and GR-S are shown in Figure 2.

EFFECT OF HANDLING AND CURING ON EXPOSURE TESTING

A study was conducted on a standard rubber extruded compound to show the effect of handling prior to molding and the effect of extrusion on exposure

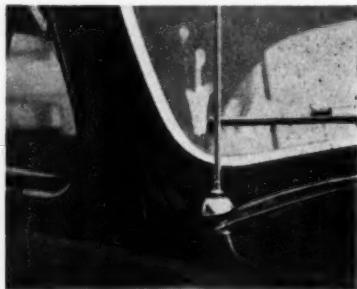


Fig. 1.—Failure of weatherstrips on a windshield.

testing. This compound, adequately protected by wax, showed that proper consideration must be given to the method of handling and curing of a given compound. It showed much poorer weather aging when molded than when it was extruded. Methods of handling prior to and during molding of this com-

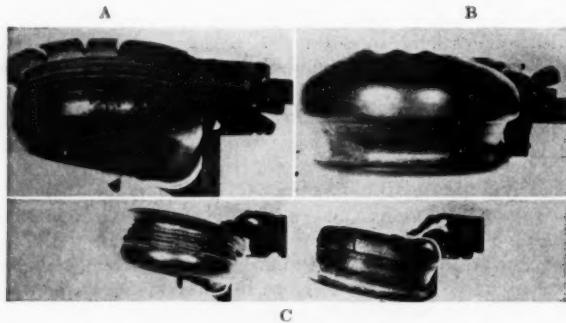


Fig. 2.—28-day exposure of commercial weatherstrips in Long Beach, California.

- A. Rubber
- B. GR-S
- C. Rubber-GR-S blend

pound have an effect on when checking begins, although ultimately failure occurred on all samples. Subsequent studies have shown that compounds of a higher quality level can be produced, not only with rubber, but especially from GR-S and Neoprene.

An extruded compound (RN 515) was sheeted on a laboratory mill and

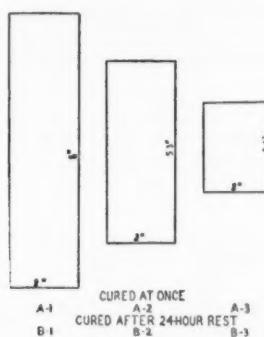


FIG. 3.—Static exposure tests on rubber molded with and without strain.

cured with and without strain immediately after removal from the mill. Stock was cut to the exact length of the cavity (8 inches) and the length was decreased to 5.3 and 2.6 inches using an equal volume of rubber (A-1, A-2, A-3, Figure 3). In this way the rubber in A-2 and A-3 was forced to flow during molding and was cured under strain. A duplicate set of cures was made (B-1, B-2, and B-3) after the milled stock was allowed to age for 24 hours.

Slabs, $\frac{1}{8} \times 2 \times 8$ inches, were mounted for static exposure testing after being shelf aged for 13 days. A small loop was formed around a $\frac{1}{4}$ -inch rod and

TABLE III
STATIC EXPOSURE TESTS

Cured Sept. 28, 1949, molded, no rest			Cured Sept. 29, 1949, molded after 24 hours' rest		
A-1	A-2	A-3	B-1	B-2	B-3
Oct. 12, 1949, 19 HOURS					
Small loop	Few faint checks	Slight checks	Slight checks	OK	Few faint checks
Large loop	OK	OK	OK	OK	OK
Series B better than series A; A-3 and B-3 worse than A-2 and B-2					
Oct. 12, 1949, 22 HOURS					
Small loop	Slight checks	Slight checks	Slight checks	Slight checks	Slight checks
Large loop	Few fine checks	Checked	Checked	OK	Checked
A-1 worse than B-1; A-2 worse than B-2; A-3 worse than B-3					
Oct. 12, 1949, 24½ HOURS					
Small loop	Checked	Checked	Checked	Checked	Checked
Large loop	Checked	Checked	Checked	OK	OK
Oct. 14, 1949, 67 HOURS					
Small loop	Checked	Checked	Checked	Checked	Checked
Large loop	Checked	Checked	Checked	OK	Few fine checks

TABLE IV
WEATHERSTRIPS EXPOSED IN CHICAGO, OCT. 11 TO NOV. 11, 1949

Weatherstrip	Tubed and cured	Rest before cure (hr.)	SAE-ASTM rating		SAE-ASTM rating		SAE-ASTM rating
			7 days	13 days	30 days		
1	Sept. 28, 1949	None	Few fine checks	1-2	Slight checkings*	2	Checked in one spot only; checking slightly intensified but not spread in area
2	Sept. 28, 1949	1	Few fine checks	1	Slight check- ing	2	Checked in one spot only; no increase after 13 days
3	Sept. 28, 1949	4	Few fine checks	1	Slight check- ing	2	Very slight check- ing in one spot only; no increase or spreading
4	Sept. 28, 1949	24	OK	0	OK	0	OK

* Weatherstrip 1 worse than 2 or 3.

nailed into position. A large loop was formed by folding the long end over to meet the end of the short loop. Table III gives the results of observations during 13-day (301-hour) and 30-day exposures.

A weatherstrip was extruded from the same batch used for molding the

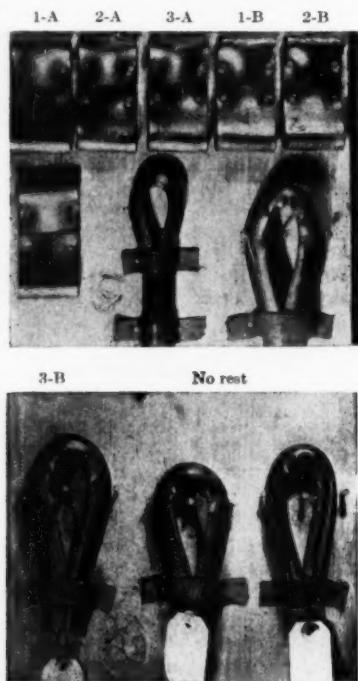


Fig. 4.—Extruded stock after cure.

slabs. The extruded stock was cured immediately and also after $\frac{1}{2}$, 4, and 24-hour rests prior to cure (Table IV). Test samples are shown in Figure 4.

Observations.—Rubber, when molded under strain, cracked faster than when cured without strain. The greater the strain the faster the rate of cracking.

Aging of the uncured stock before molding decreased cracking. Aged uncured stock, when cured under strain, cracked when exposed to sunlight, but at a slower rate than when fresh stock was used.

Aging of extruded stock before cure decreased cracking on outdoor exposure.

An extruded compound showed a much greater tendency to check or crack when molded and exposed under the described conditions.

This extruded stock contains strains which do not disappear during cure unless the uncured stock has been sufficiently aged prior to cure. Extruded stock aged 24 hours prior to cure gave excellent results on static exposure testing, whereas stock aged 4 hours or less before curing still contained residual strains and therefore cracked on static exposure.

Several factors should be observed to ensure elimination of as many variables as possible in the preparation and evaluation of test samples. Such steps are also of major importance in establishing uniform production procedures. The factors to be observed vary with the compound and equipment that is being used, but having once determined what they are, the procedure should be carefully observed. The higher the quality of the natural rubber or GR-S compound the less effect some of these variables seem to have on weather aging. Unless these factors are controlled and a uniform test procedure is used, it is almost impossible for two observers to check with each other, particularly on outdoor aging in different locations.

VARIABLES IN EXPOSURE TESTING

The variables to be considered in preparing samples for exposure testing are:

1. Masterbatches.
2. Selection of polymers—rubber, GR-S, Butyl, and Neoprene.
3. Effect of dispersion, cleanliness, and impurities.
4. Selection of wax.
5. Aging of mixed stock.
6. Aging of prepared stock before curing.
7. Cure stock with minimum flow in mold.
8. Effect of lubricants on molded and extruded stocks.
9. Effect of methods of molding—compression, injection, and transfer.
10. Effect of cure.
11. Aging of samples before mounting for exposure tests.
12. Not bending or distorting samples during exposure.

SAE-ASTM EXPOSURE TEST METHOD

A method of preparing, mounting, and rating samples for laboratory or outdoor exposure tests has been developed by section IV-P of the SAE-ASTM Technical Committee on Automotive Rubber¹⁴. It makes possible the correlation of exposure tests between various laboratories.

A triangular test-specimen, 10 inches long, of molded, extruded, or sponge rubber, is cured in a straight position. It is recommended that the technologist

observe a minimum rest period of 24 hours between stock mixing and stock preparation and a minimum rest period of $\frac{1}{2}$ hour between stock preparation and curing when preparing specimens.

Bench marks are placed on the specimen with crayon, $7\frac{1}{2}$ inches apart ($1\frac{1}{4}$ inch from ends). The specimens are formed into a loop by placing the ends together and tying securely with wire at bench marks. The loop is slipped over the mandrel. After the specimens have been mounted, they are rested for a minimum of 48 hours at room temperature in a relatively ozone-free atmosphere. This allows time for the wax film, which may have cracked during mounting, to reform. Production samples may be prepared and exposed in a similar manner.

The degree of cracking is rated according to the following system, considering only the size of the cracks and not the number of cracks formed.

Rating number	Description (Figures 5 and 6)
0	No cracking visible at $2 \times$ magnification
1	No cracking visible at $1 \times$ magnification, but visible at $2 \times$ magnification
2	Small cracking visible at $1 \times$ magnification
3	Medium-sized (or larger) cracking

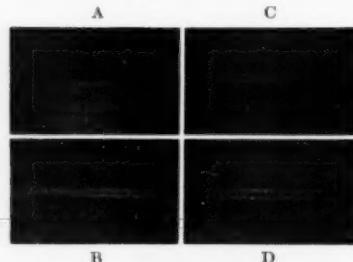


FIG. 5.—Ratings for weathering tests ($2 \times$).

- A. 0
- B. 1
- C. 2
- D. 3

Figures 5 and 6 illustrate the rating method which has been adopted for static exposure tests. Figure 5 is a photograph of a portion of the sample and Figure 6 is a photograph of the sample on the mandrel.

A GR-S compound was molded in a triangular section and tested in an ozone chamber, which contained 30 parts of ozone per 100,000,000 parts of air, for 70 hours at 100° F. It was also tested on a 2-inch mandrel in Florida for 30 days and in Chicago for 49 days. Figure 7 shows that the ozone chamber produced the most cracking, followed by Florida and then Chicago. All three samples show the same tendency toward deep cracking. The ozone chamber, therefore, produces the same type of cracking in a short period of time that occurs in Florida and Chicago only after a prolonged period of exposure.

In order to establish reproducibility and reliability of exposure tests on the triangular section, 30 pieces, 8 feet long, were extruded from a natural rubber and a GR-S extruded compound. Samples from each of the 30 pieces were exposed in the ultraviolet arc chamber at Miami and Chicago. The results show

very little difference between the various samples. The order of extrusion has no effect on the exposure test results.

Natural rubber and GR-S compounds were extruded, and injection-, compression-, and transfer-molded, in the triangular section IV-P die. Tests

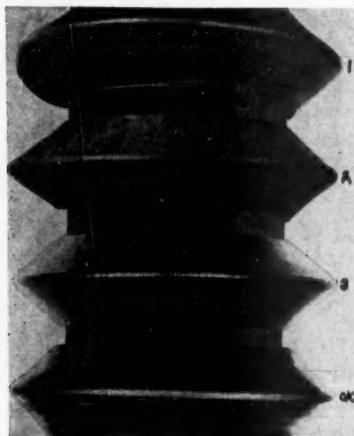


FIG. 6.—Rating system on a triangular test piece.

were made on samples aged 48 hours after mounting on a 2-inch varnished wood mandrel prior to exposure (Figure 8). On medium quality compounds a longer rest period before exposure is beneficial. There was no substantial

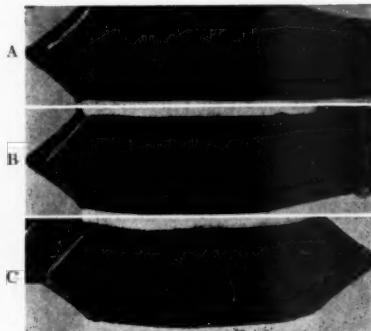


FIG. 7.—Exposed triangular section of GR-S.

- A. Chicago, Oct. 30-Dec. 18, 1950
- B. Florida, Nov. 8-Dec. 8, 1950
- C. Ozone chamber, 70 hours at 100° F.

difference between rubber and GR-S regardless of the method of molding or curing when tested in the Pontiac ozone box, or at Miami and Chicago (Table V). GR-S gave less cracking than natural rubber in the Crabtree-Kemp ozone chamber. Cracking was increased when strains were introduced during

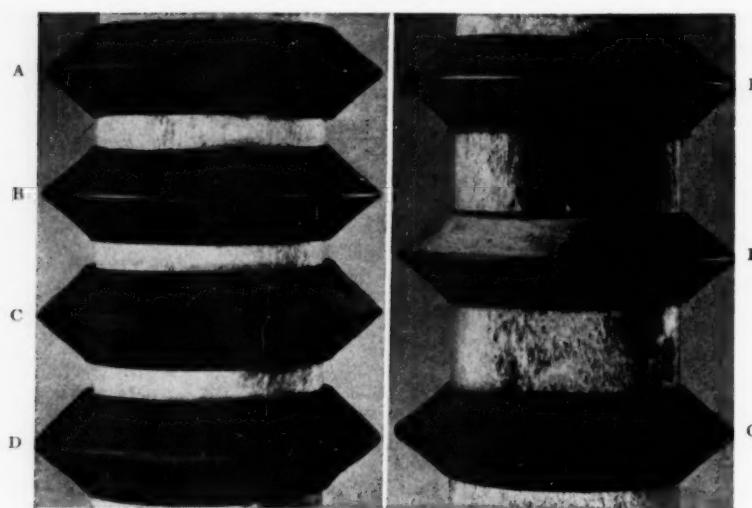


FIG. 8.—60-day exposure of natural rubber and GR-S in Florida.

A. 69070, injection	E. 69070, compression
B. 938347, injection	F. 69070, transfer
C. 69070, extruded	G. 938347, transfer
D. 938347, extruded	

TABLE V
EXPOSURE TESTING OF GOOD QUALITY NATURAL RUBBER
AND GR-S COMPOUNDS

Tested	(Two-inch mandrel) Rubber				GR-S			
	Extruded	Inject- ion	Com- pression	Transfer	Ex- truded	Inject- ion	Com- pression	Transfer
Pontiac ozone box, 138 hr. at room temp.	OK	OK	OK	OK	OK	OK	OK	OK
Crabtree-Kemp box, 128 hr. at 100° F*	3	3	2	2 and 0	2	OK	OK	1 and 0
Crabtree-Kemp box, 128 hr. at 100° F, naphtha- washed	3 and 4	2	2	4 and 0	2	2	2	2
Heated 15 min. at 158° F	4	OK	OK	2	2	1	2	0
Heated 2 hr. at 158° F	4	3	3	4	2	2	1	2 and 1
Florida, 60 days, July and August 1950	OK	OK	OK	OK	OK	OK	OK	OK
Florida, 60 days, Sept. 11- Oct. 17, 1950, and Oct. 20-Nov. 14, 1950	1	0	—	1	1	1	OK	OK
Chicago, 91 days, Aug. 22-Nov. 21, 1950	OK	1	—	OK	OK	OK	OK	OK

* 30 to 35 parts of ozone per 100,000,000 parts of air.

injection and transfer molding. Washing with naphtha before exposure in the Crabtree-Kemp box was harmful to GR-S except when extruded, but on natural rubber the effect was slight (except for one sample transfer molded).

Heating 15 minutes at 158° F before exposure in the Crabtree-Kemp ozone chamber decreased cracking on injection- and compression-molded, natural rubber samples, but had no effect on the transfer-molded, although cracking was increasing on the extruded sample. Heating for a longer period (2 hours) was harmful. Heating 15 minutes at 158° F increased cracking on the injection- and compression-molded GR-S, while the extruded and transfer-molded samples were unchanged.

EFFECT OF DISPERSION ON WEATHER AGING

Cracking is produced or accelerated by various causes, such as grit¹⁶, foreign matter, impurities, and poor dispersion. It is frequently possible to

TABLE VI
DISPERSION STUDIES ON EXPOSED SAMPLES

Compd.	Date	Days	Figure	Rating (old method) Cure, minutes			
				5	10	15	20
Exposure in Chicago							
2	Jan. 4, 1950	165	9A	6	6	6	7
135	Jan. 4, 1950	165	9B		3		2
510	March 30, 1950	36	9C	4	4	4	4
511	March 30, 1950	36	9D	3	4	4	4
513	March 30, 1950	36	9E	4	4	3	3
Exposure in Miami							
2	Dec. 29, 1949	30	9A	5	7	7	7
			9B		2		2
510	March 29, 1950	30	9C	7	7	7	5
511	March 29, 1950	30	9D	6	7	7	7
513	March 29, 1950	30	9E	4	4	3	3
Rating (SAE-ASTM)							
Exposure in Chicago							
515	May 9, 1950	7	10A		3+		
516	Jan. 28, 1950	207	10B		1 to 2		
517	March 13, 1950	162	10C		1		
518	March 13, 1950	162	11A		1		
Exposure in Miami							
515	May 23, 1950	30	10A		3		
516	May 23, 1950	30	10B		1 to 2		
517	May 23, 1950	30	10C		0 to 1		
518	May 23, 1950	30	11A		1 to 2		
	July and August 1950	60	11B		0		

predict the weather aging of a rubber compound by observing the type of dispersion. The presence of grit, lumps, and agglomerates at the surface results in a strained condition that will produce cracks. Through the cooperation of B. R. Silver, the New Jersey Zinc Company laboratories prepared Roninger dispersion photomicrographs of compounds which had been exposed in Chicago and Miami (Table VI). The purpose in making these photomicrographs was to determine if there is any relationship between dispersion and weather aging. The photographs shown in Figure 9 are of compounds with the same content

of natural rubber, carbon black, sulfur, and accelerator, the only change being in wax and stearic acid. The figures which show the best dispersion also gave the best weather aging. Samples shown in Figure 9A and B were exposed 30 days in Florida; A shows better dispersion and also gave better weather aging. The samples shown in Figure 9C, D, and E were exposed simultaneously, and

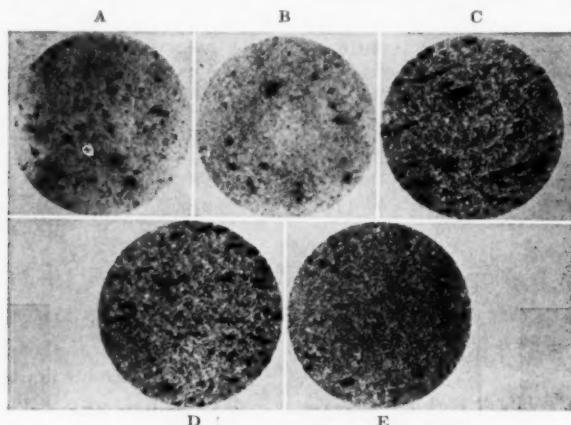


FIG. 9.—Photomicrographs of exposed rubber compounds of same composition, 30-day exposure in Florida.

Figure 9E shows the best dispersion and weather aging. All photomicrographs are at 500 magnification.

Figure 10 represents three natural-rubber compounds, which vary in composition and dispersion characteristics. The compound illustrated in Figure 10A, although containing an ample amount of wax, consistently showed poor weather aging and dispersion, whereas the compound in Figure 10B showed an

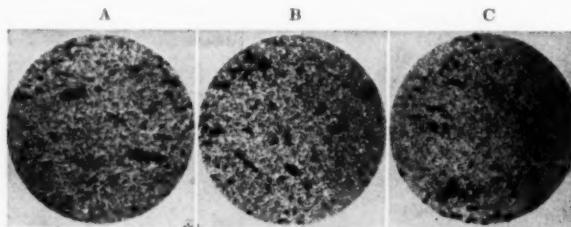


FIG. 10.—Photomicrographs of exposed rubber compounds of different compositions.

improvement in this respect. The sample shown in Figure 10C showed good dispersion and also gave good weather aging.

A GR-S compound that has given a weather-aged rating in Chicago and Florida of 1 and 2 instead of 0 as expected is shown in Figure 11A. The dispersion is extremely poor, and better results should be obtained with improved dispersion. In Figure 11B is shown a GR-S compound that has consistently given a 0 to 1 rating in the ozone chamber, as well as outdoors in California,

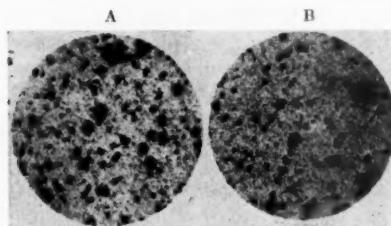


FIG. 11.—Photomicrographs of exposed GR-S compounds.

A. Rating of 1 in Chicago, 2 in Florida
 B. Rating of 0 to 1 in ozone chamber, and in
 Florida, California, and Illinois

Illinois, and Florida. The dispersion is still not very good, but it is much better than the sample shown in Figure 11A. Better results would be anticipated if the dispersion of this stock were improved.

GR-S-101 is a low-temperature rubber, also available as a masterbatch GR-S-X-580, containing 55 parts of Philblack 0 on 100 parts of GR-S-101. GR-S-101 and X-580 have been compared in a GR-S extruded compound.

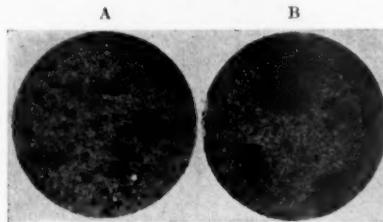


FIG. 12.—Dispersion in GR-S.

A. X-580
 B. X-101

This gave a comparison between carbon black added on a laboratory mill *vs.* a carbon black slurry added to the GR-S latex. Figure 12 shows that a much better dispersion was obtained with GR-S masterbatch X-580 (Figure 12A). Exposure tests show much better weather aging and less cracking with X-580 (Figure 13). The exposure rating is presented in Table VII.

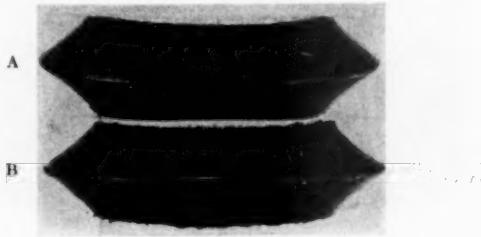


FIG. 13.—Exposure in GR-S.

A. X-580
 B. X-101

TABLE VII
EXPOSURE RATING*

	Chicago, May 2- June 2, 1951 (31 days)	Miami, May 8- June 7, 1951 (30 days)	Ozone chamber, 70 hr. at 100° F. 25 parts/100 million
GR-S-101	3	3	3
GR-S-X-580	0	2	0

* Shown in Figure 13.

In Chicago GR-S-101 showed bad cracking in 3 days. It gave a rating of 1 in 4 hours and a rating of 2 in 14 hours in the ozone chamber. The GR-S masterbatch with improved dispersion is much superior in exposure testing.

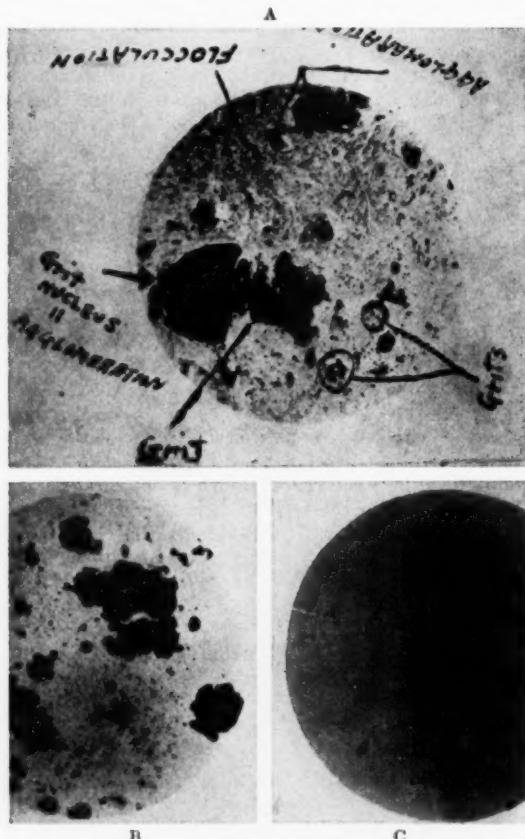


FIG. 14.—Effect of agglomerates and grit on natural rubber under strain.

- A. 45 parts of EPC, 100 parts of natural rubber
- B. 45 parts of residue, 100 parts of natural rubber
- C. Carbon black dispersion

The presence of agglomerates and grit in EPC carbon black dispersions in natural rubber may cause points of weakness when exposed under strain. Figure 14A illustrates the presence of grit, agglomerates, and flocculation at 500 magnification of 45 parts of EPC carbon black on 100 parts of natural rubber. Figure 14B shows the dispersion obtained by incorporating 45 parts of the residue collected on a 325-mesh screen on 100 parts of rubber. A carbon black dispersion which still shows a few small areas of grit at 500 magnification is shown in Figure 14C. In order to obtain the best weather aging it is desirable to eliminate grit and agglomerates to ensure good dispersion.

The effect of various dispersing agents used in the preparation of carbon black slurries for GR-S masterbatches on cracking of rubber has been studied (Table VIII). This study was undertaken to determine the effect of any residual dispersing agent retained in the GR-S masterbatch.

TABLE VIII
VARIOUS DISPERSING AGENTS IN GR-S-26
(Triangular and SAE-ASTM rating; control = 0)

Material	Rating, Chicago ^a			Rating, Miami		
	Dispersing agent Parts/100 GR-S			Dispersing agent Parts/100 GR-S		
	1	3	5	1	3	5
Chestnut extract	1-2	1-2	1	3	3+	1
Daxad-11	1	3	1	1	2	3+
Indulin-A	1	1	2	1	3+	3
Triton R-100	1	2	2	2	2	2
Marasperse-CB	1	1	1	1	1	1
Silvacon-490	1	3	1	2	2	2
Sodium hydroxide	2			2		
Lomar-PW	1	1	1	2	2	2
Indulin-C	1	0	0	2	2	2
Masonoid-D	2	3	3	2	3	3+

^a Exposed 83 days, May 2 to July 27, 1951.

^b Exposed 30 days, May 8 to June 7, 1951.

One, three, and five parts of dispersing agent were added to 100 parts of GR-S-26 on a laboratory mill in an extruded compound¹⁶. Triangular strips were molded and exposed 30 days in Miami and 83 days in Chicago. In Florida all materials except Marasperse CB adversely affected cracking of the GR-S. In Chicago Marasperse CB, Lomar PW, and Indulin C did not affect weather aging of GR-S. Triton R-100 and Masonoid D adversely affected cracking of GR-S. The remaining materials have only a slight effect.

PROTECTIVE WAXES IN NATURAL RUBBER AND GR-S

Rubber and GR-S compounds require the use of a protective wax to give good weather aging, although wax alone will not ensure good weather aging. Unless a wax blooms and continues to bloom to the rubber surface no protection results. Surface protection by addition of waxes which bloom to the surface was suggested in 1881¹⁷. Microcrystalline waxes, which are an essential component of a good wax when used alone, do not bloom to the rubber surface in sufficient quantity to afford adequate protection. It is, therefore, common practice to blend these waxes with paraffin or low melting microcrystalline waxes to give a satisfactory bloom. The flexibility of the wax film and the

type of bloom are important. It is often possible to predict the weather-aging properties of a compound by observing the nature of the bloom.

There is strong evidence that a linear chain is superior to a branched-chain hydrocarbon. Microcrystalline waxes vary widely in quality. A major application for microcrystalline waxes is based on their electrical properties. Waxes with satisfactory electrical properties are preferred in rubber, and they should be evaluated in various locations at all seasons of the year. A wax which gives good results in Chicago, Ill., may not give good results in Florida.

A microcrystalline wax was fractionated in order to determine if any of the fractions imparted superior weather aging. The various fractions were tested in a compound composed of:

	Parts
Smoked sheet rubber	100
EPC black	40
638½	5
Stearic acid	2
Zinc oxide	5
Altax	1
Sulfur	2.5
Wax	10

and the results are presented in Table IX.

There is evidence that the lower the melting point of the microcrystalline wax, the better the weather aging; blending of the fractions with paraffin improves weather aging. In Chicago there was no difference between the various wax blends, but in Florida the lower melting fractions gave better weather aging than the higher melting fractions.

TABLE IX
FRACTIONS OF MICROCRYSTALLINE WAX
(Old method of rating)

Melting Pt., °F		Jan. 4- Feb. 6, 1950,		Dec. 29- Jan. 28, 1950,	
		Cure 10 min.	Cure 20 min.	Cure 10 min.	Cure 20 min.
		Microcrystalline wax fractions			
L 8617 and L 8618	177, 168	7	7	7	7
L 8619	156	7	7	6	7
L 8620	148	6	6	6	6
L 8621	140	6	6	5	6
L 8622 and L 8623	134, 125	4	5	4	4
75% Microcrystalline wax blended with 25% paraffin at 130° F					
L 8617 and L 8618		3	3	6	6
L 8619		3	3	5	5
L 8620		3	3	2	3
L 8621		3	3	4	4
L 8622 and L 8623		3	3	4	4

Correlation of old method of rating with SAE-ASTM rating system

Old method	SAE-ASTM rating
2	1
3	2
4	3
5, 6, 7	3 plus

A paraffin wax, melting point 130° F., was fractionated into fractions melting as follows: 114°, 120°, 126°, 130°, 136°, and 140° F. These fractions were blended in the proportion of 75 per cent Superla Wax and 25 per cent paraffin fraction. Evaluation of these waxes in rubber showed no difference in Chicago, but in Florida showed an advantage for the higher melting paraffin fraction.

Observations were made as to whether an under- or overcure shows more cracking over a range of 5-, 10-, 15-, and 20-minute cures at 316° F. In Chicago there were 145 compounds that showed no difference in cracking between various cures. Forty-three compounds cracked worse on the 20-minute cure; 30 cracked worse on the 5-minute or shorter cure. In Florida where conditions were more severe, there were 111 compounds on which the 20-minute cure cracked more than the short cures, although 20 compounds cracked more on the 5-minute cure. There were 92 compounds in Florida that showed the same degree of cracking on all cures.

After vulcanization, some waxes bloom to the surface more slowly than others. In general, the long cure of 20 minutes always blooms before the shorter cures. When a wax blooms to the surface quickly no difference is noted between appearance of bloom on the 5- and 20-minute cures. After shelf aging of slabs, the shorter cure of 5 minutes develops the heaviest bloom with most waxes.

There are a number of pyrrole compounds that provide protection against ozone¹⁸, but they are not used commercially. The presence of a chemical protective agent in the wax constitutes the next advance in improved weather aging of rubber products. NBC (du Pont) is recommended as a good protective material for GR-S, but not for rubber.

EFFECT OF SOME COMPOUNDS ON WEATHER AGING

Thomson and Lewis¹⁹ first called attention to the harmful effect of iron, copper, and manganese on rubber. The effect of iron salts has been studied by a number of investigators²⁰. Albert, Smith, and Gottschalk²¹ showed that soluble iron decreases the resistance of GR-S to aging more than copper or manganese. The deterioration of rubber containing copper and manganese has been widely observed²².

Because iron, copper, and manganese are frequently present in rubber and various compounding ingredients, it was deemed advisable to study the effect of some of their soluble salts on cracking of rubber. At times a good weather aging compound shows premature cracking for no known reason.

Water-soluble salts of iron and manganese and copper stearate, which was soluble in many organic solvents, were used. The present observations are based solely on the particular salts used. Insoluble manganese, copper, and iron compounds have not been investigated in a good weather-aging compound. Van Rossem and Talen⁴ found that iron and copper compounds have no influence on formation of cracks in rubber. In a GR-S compound not protected by wax, copper dimethyldithiocarbamate and zinc dimethyldithiocarbamate, as activators, show no difference in cracking. Unprotected compounds crack in a matter of a few hours.

Sufficient quantities of manganese sulfate, copper stearate, ferrous and ferric sulfate were added to a good weather-aging natural rubber and GR-S compound adequately protected by wax to give 0.05, 0.005, and 0.0005 part of each metal per 100 parts of rubber hydrocarbon. Triangular strips were molded and exposed in duplicate in Chicago, Miami, and in an ozone chamber.

Natural rubber.—The metallic salts adversely affected cracking of the rubber, regardless of the amount added, when exposed for 60 days (December 17, 1950, to February 15, 1951) in Miami.

After 22 days' exposure in Chicago, 0.05 part of each metal caused cracking, while the control was uncracked. Manganese (0.005 part) had no effect; the other metals caused cracking. At 0.005 part of metal only ferric sulfate caused cracking. After 220 days' exposure all samples were as good or better than the control.

After 70 hours of exposure at 100° F in the ozone chamber (30 parts ozone per 100,000,000 parts of air), manganese had no effect on cracking, copper and ferric iron caused the same degree of cracking, and ferrous iron caused the most severe cracking. Ferrous iron and copper gave a cracking rate of 1 and 29 in 5 hours, respectively.

GR-S.—The metallic salts adversely affected cracking of the GR-S, regardless of the amount added, when exposed for 60 days (December 17, 1960, to February 15, 1951) in Miami.

After 22 days' exposure in Chicago, all samples except copper (0.0005 part) were cracked; the control was still uncracked. After 220 days there was no appreciable difference between any of the samples.

After 70 hours' exposure in the ozone chamber at 100° F, manganese (except 0.05 part) and ferrous iron accelerated the cracking of GR-S, but after 70 hours of exposure the samples rated the same as the control. Copper and ferric iron accelerated the cracking of GR-S; ferric iron accelerated the cracking so that a rating of 1 was obtained in 2 hours.

These preliminary observations indicate that these metallic salts accelerate the cracking of a natural rubber and a GR-S weather-aging compound; their presence, therefore, is to be avoided. Prolonged exposure in Chicago showed no adverse effect of these salts. Results of the described tests are presented in Table X.

Copper, manganese, and iron naphthenates were added to a natural rubber and a GR-S weather-aged extruded compound. A sufficient amount of each compound was added to give 0.05, 0.005, and 0.0005 part of the metal per 100 parts of rubber hydrocarbon. Samples were exposed in duplicate in Chicago and Miami. After a 48-day exposure in Chicago, none of the naphthenates adversely affected weather aging (Table XI). After 30 days in Miami, copper naphthenate had no effect on rubber or GR-S; manganese naphthenate accelerated cracking of natural rubber, but had little or no effect on GR-S. Iron naphthenate accelerated the cracking in both natural rubber and GR-S.

Neoprene gave better weather aging than natural rubber or GR-S in carbon black-loaded compounds. Thompson and Catton²³ have emphasized that Neoprene must be properly compounded to obtain good weather aging. The percentage of Neoprene by volume should not be less than 50 for best results. Clay gave the best results of the mineral fillers; whiting at all loadings adversely affected outdoor aging. Substitution of GR-S or natural rubber for Neoprene adversely affected weather aging (natural rubber was more detrimental than GR-S).

Butyl rubber when properly compounded and adequately protected by wax will give good weather aging. The Midwest Rubber Reclaiming Company²⁴ has completed some weathering tests which emphasize the importance of dispersion. When reclaimed Butyl is added to GR-S by a special mixing technique, there was no checking after a 90-day outdoor exposure in Barberton,

TABLE X
EFFECT OF METALLIC SALTS ON CRACKING OF MOLDED RUBBER AND GR-S

	Rating (60-day exposure, Miami ^a) Metal/100 Rubber, %	Rating (22-day exposure, Chicago ^b) Metal/100 Rubber, %	Rating (220-day exposure, Chicago ^c) Metal/100 Rubber, %	Rating (Ozone chamber at 100° F.) Metal/100 Rubber, %			Rating (Ozone chamber for 70 hr. at 100° F.) Metal/100 Rubber, %	Rating (Ozone chamber for 70 hr. at 100° F.) Metal/100 Rubber, %
				0	0.05	0.005		
Molded Rubber (88-37)								
Control	1	0	3	50	50	50	1	1
Manganese	2	2	2.5	1	0	0	1	1
Copper	2	2	2	1	1	1	2	2
Ferrous iron	2	2	2	1	1	1	3	3
Ferric iron	2	2	2	2	1	1	2	2
Molded GR-S (44-65)								
Control	1	0	1-2	50	50	50	1	1
Manganese	2	2	2	1	1	1	1	1
Copper	2.5	2	2	1	0	1	2	2
Ferrous iron	2	2	2	1	1	1	1	1
Ferric iron	2	2	2	1	1	1	2	3

^a Dec. 17, 1950, to Feb. 15, 1951.^b Dec. 19, 1950, to Jan. 10, 1951.^c Dec. 19, 1950, to July 27, 1951.^d 30 parts of ozone per 10,000,000 parts of air; for a number of hours to give a rating of 1.^e 30 parts of ozone per 100,000,000 parts of air; SAE-ASTM rating.

TABLE XI

EFFECT OF NAPHTHENATES ON CRACKING OF RUBBER AND GR-S

Naphthenate	0	Rating, Chicago ^a Metal/100 Rubber			Rating, Florida ^b Metal/100 Rubber		
		0.05	0.005	0.0005	0	0.05	0.005
Rubber (88-37)							
Control	2				0		
Copper		1	2	2		0	1
Manganese		2	1	1		1	0
Iron		2	2	3		2	1
GR-S (44-65)							
Control	2				0		
Copper		1	1	1		0	0
Manganese		1	2	1		0	0
Iron		2	1	2		1	1

^a Exposed 48 days, Jan. 17 to March 6, 1951.^b Exposed 30 days, Jan. 24 to Feb. 23, 1951.

Ohio, whereas compounds mixed according to ordinary technique show checking and cracking (Tables XII and XIII).

SPONGE RUBBER

A comparison of Butyl rubber, Neoprene, and GR-S in the applied skin of sponge rubber has been made by Yoran²⁵, who found that the thickness of the applied skin is important, although it does not appear to be as important with Neoprene as with GR-S and rubber. A Butyl cover is unsatisfactory, regardless of the thickness of the applied skin (0.010-, 0.017- or 0.027-inch gage).

TABLE XII
BUTYL RECLAIM AND GR-S BLENDS

Compound	A	B	B-1 ^a Parts		C	C-1 ^a
GR-S	100	75	75	50	50	
Butex	—	44	44	88	88	
Cumar-MH	20	20	20	20	20	
Process oil	16	15	15	15	15	
Stearic acid	1	1	1	1	1	
Heliozone	5	5	5	5	5	
Philblack-A	55	55	55	55	55	
Hard clay	20	20	20	20	20	
Zinc oxide	5	5	5	5	5	
Accelerator A ^b	1.5	1.5	1.5	1.5	1.5	
Accelerator B ^c	0.1875	0.1875	0.1875	0.1875	0.1875	
Sulfur	2	3	2	2	2	
Total	224.6875	243.6875	243.6875	262.6875	262.6875	
Specific gravity	1.18	1.21	1.21	1.23	1.23	

^a Special mixing technique used.^b Accelerator A, benzothiayl disulfide.^c Accelerator B, copper dimethylthiocarbamate. [?]

TABLE XIII
90-DAY EXPOSURES IN BARBERTON, OHIO
(June 2 to Aug. 31, 1950)

Compd.	Time of cure at 316° F (min.)	Days for rating of 1	Days for rating of 2	Rating on Aug. 31
A	12	53	—	1
	18	—	—	0
B	12	—	—	0
	18	10	14	2
B-1 ^a	12	—	—	0
	18	—	—	0
C	12	60	—	1
	18	7	14	2
C-1 ^a	12	—	—	0
	18	—	—	0

^a Special mixing technique used.

TABLE XIV
Lafayette, Ind., 30-day exposure
Aug. 10-Sept. 9, 1950

SAE-ASTM section	Gage (in. $\times 10^3$)	Rating
Butyl cover	10	3
	17	3
	27	2
Neoprene-W	10	0
	17	0
	27	0
GR-S	10	3
	17	0
	27	0
GR-S, no wax	10	3
	17	3
	27	3
GR-S, under- cure	10	2
	17	0
	27	0
GR-S, no wax and undercure	10	3
	17	0
	27	0

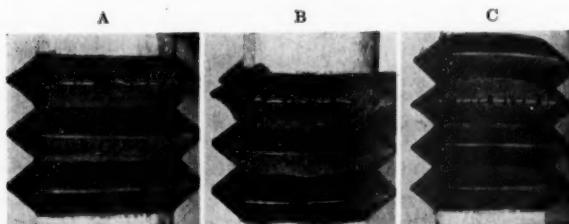


FIG. 15.—Effect of Butyl rubber, Neoprene, and GR-S on sponge rubber.

- A. 0.010-inch gage
From top to bottom, Butyl, Neoprene-W, and GR-S
- B. 0.017-inch gage
From top to bottom, Butyl, Neoprene-W, and GR-S
- C. From top to bottom, no wax and undercured; no wax; undercured; and GR-S regular

Neoprene is satisfactory at a gage of 0.010-inch, whereas GR-S is not satisfactory unless a gage of 0.017-inch is used (Table XIV and Figure 15).

An undercure improves the weathering resistance of GR-S, but the presence of a protective wax is still essential. Outdoor exposure test results were confirmed in the Crabtree-Kemp ozone chamber.

SUMMARY

Deterioration of rubber products on outdoor exposure is due to the action of sunlight and ozone. Ozone cracking results when rubber is exposed under strain. The type of cracking produced by ozone is not produced by other elements or materials normally present in the atmosphere. Light-energized oxidation produces a crazed condition on the surface of the rubber, which is quite different from the effects produced by ozone. This study was undertaken to determine the factors which influence the resistance of rubber products to ozone. It was found that rubber cured under strain cracks faster than when cured at rest. Manufacturing defects, such as blisters, air traps, foreign matter, and pigment agglomerates, resulted in premature cracking. Certain manganese, copper, and iron salts had an adverse effect on ozone resistance in outdoor and accelerated exposure tests. Some dispersing agents used to make carbon black slurries for GR-S carbon black masterbatches, showed an adverse effect on weather aging. The selection of a polymer, such as natural rubber, GR-S, Neoprene, or Butyl rubber, has a marked influence on the ozone resistance of automotive rubber products. Unless a polymer is handled and compounded properly, good ozone resistance is not obtained. In outdoor exposure the effect of sunlight, ozone, heat, and water varies seasonally in Florida, California, Michigan, and Illinois. Many tests and much good judgment must be exercised in correlating accelerated and outdoor exposure tests.

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OZONE DETERIORATION OF ELASTOMERIC MATERIALS

PRELIMINARY RESULTS OF A STUDY BY INFRARED SPECTROSCOPY *

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The isolation and identification, by conventional chemical methods, of the products of ozone attack of natural and synthetic rubberlike materials have been intensively investigated by several workers¹. The procedures involved are generally intricate and long drawn-out. The present studies were undertaken to explore the feasibility of employing the relatively simpler method of

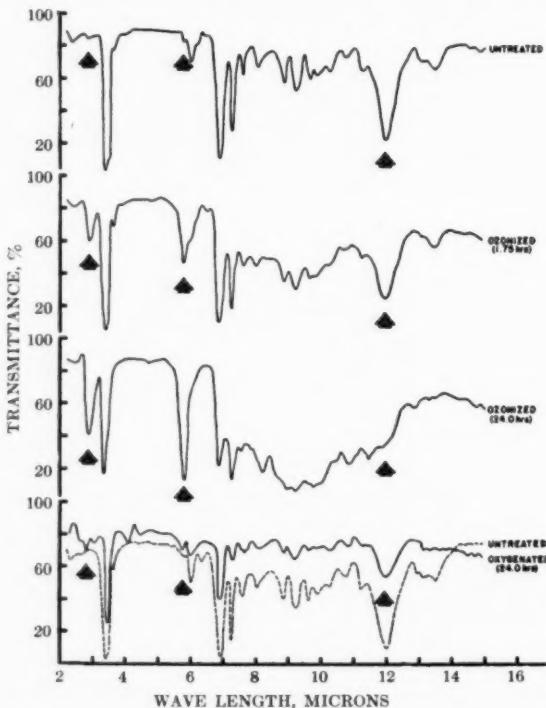


FIG. 1.—Relative effects of ozonation and oxygenation of 1 per cent solutions of Hevea (smoked sheet) in ethylene dichloride.

* Reprinted from *Analytical Chemistry*, Vol. 24, No. 4, 630-635, April 1952. This paper was presented before the Division of Rubber Chemistry at its meeting in Washington, D. C., February 28-March 2, 1951.

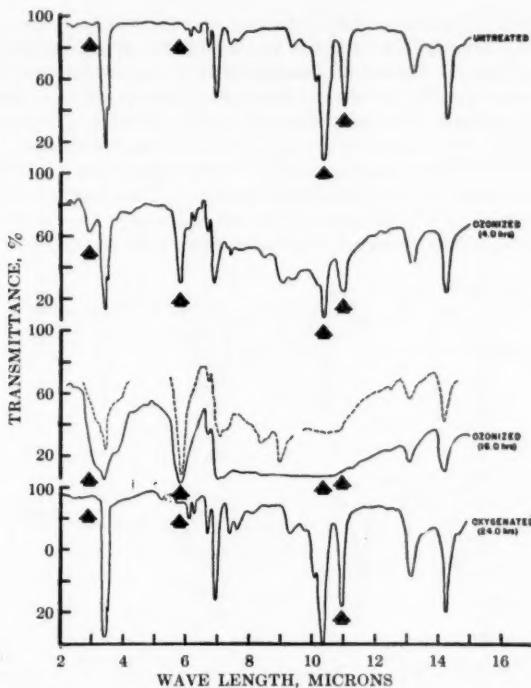


FIG. 2.—Relative effects of ozonization and oxygenation of 1 per cent solutions of GR-S (41° polymer) in *o*-dichlorobenzene.

infrared spectroscopy to determine compositional changes affected by ozonization of materials of this type. The ultimate objective is the development of a practical method, more fundamental in nature than those currently in use², for the accelerated evaluation of ozone aging of elastomer compounds.

In this paper, the initial results presented are concerned exclusively with the examination of the various elastomers in the crude or raw gum state. The polymers were ozonized by the solution method³, and were prepared for infrared spectrographic analysis by the technique developed by Dinsmore and Smith⁴. Essentially, the procedure followed was:

Purification.—The specimen was extracted with acetone (when not excessively gelled by that solvent) and 95 per cent ethyl alcohol to remove antioxidant and residual emulsifying or polymerization agents.

Solution.—The purified polymer was dissolved in a chlorinated hydrocarbon solvent. Ethylene dichloride and *o*-dichlorobenzene were found satisfactory. The latter, being less volatile, was preferred. The concentration of the solution, before ozonization, was adjusted to contain 1 gram of polymer per 100 cc. of solvent.

Ozonization.—Ozonized oxygen, containing approximately 50 p.p.m. of ozone as determined by periodic iodometric titration, was bubbled at the rate of 0.5 liter per minute through 100 cc. of the polymer solution at room temperature. The ozone was generated by passing commercial tank oxygen over an

ultraviolet lamp (Hanovia Safe-T-Aire type). The resultant oxygen-ozone mixture was led directly through glass tubing 0.5 cm. in inside diameter into the body of the solution. The use of absorption aids, such as bubble towers, fritted disks, etc., was purposely avoided to minimize decomposition of the ozone. At regular predetermined intervals, aliquots of the solution continuously undergoing ozonization were removed for treatment as described below.

Evaporation.—Where small amounts of precipitate formed during ozonization, these were removed by careful decantation. The clear solution was gently warmed just below the boiling temperature of the solvent, until a sirupy viscous concentrate of the ozonized elastomer was obtained.

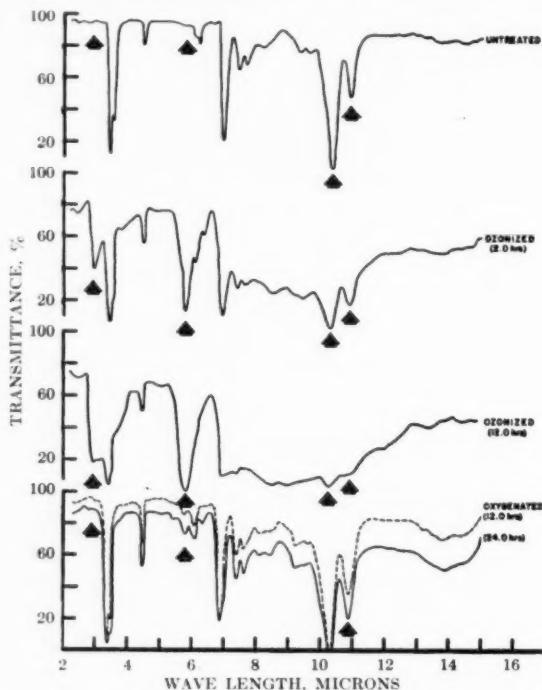


FIG. 3.—Relative effects of ozonization and oxygenation of 1 per cent solutions of nitrile rubber (Paracril 26 N) in *o*-dichlorobenzene.

Film spreading.—A film of the ionized product was cast by spreading a layer of the concentrate on a rock salt plate and evaporating to a solvent-free state in a vacuum oven at 50° C. Films of increased thickness could be obtained by several such depositions on a single plate.

Spectrographic examination.—Spectral data on the films thus cast were obtained in the 2- to 15-micron region, using a Beckman Model IR-2 infrared recording spectrophotometer.

For purposes of comparison, spectrograms were also obtained on films from the polymer solutions prior to ozonization, and on films in the preparation of which the ozonization step was replaced by treatment with unozoneized oxygen.

Figures 1 to 5, inclusive, show results of application of the above procedure to Hevea (smoked sheet); GR-S (cold rubber, 41° ploymer); nitrile rubber (Paracril 26 N); Neoprene Type W; and Butyl rubber (GR-I). Although a series of at least six aliquots was examined for each polymer solution during a 24-hour ozonization period, the two ozonization spectra selected show the trend of the gross changes observed.

The arrows point to significant absorption bands. At 2.9 microns, absorption is generally considered to reflect hydroxyl (OH) group content. In the region of 5.8 microns, absorption indicates carbonyl (C=O) group, whether of carboxylic, aldehyde, or ketone origin. At higher wave lengths, the arrows,

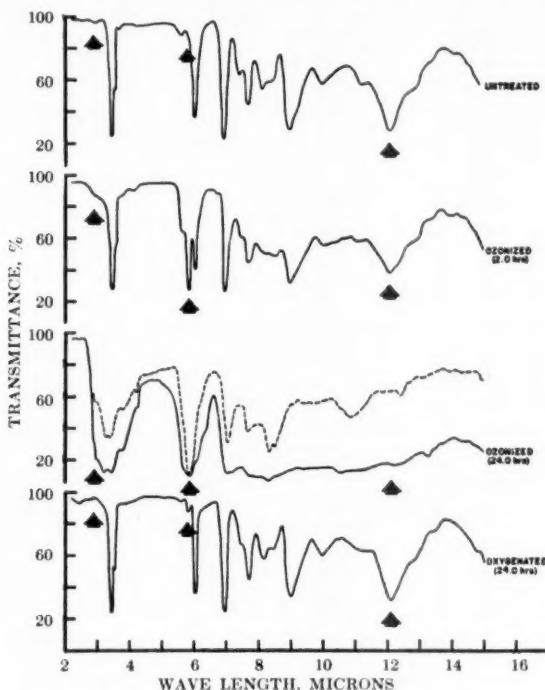


FIG. 4.—Relative effects of ozonization and oxygenation of 1 per cent solutions of Neoprene type W in *o*-dichlorobenzene.

where present, designate bands that are characteristic of the polymer at the double bond. In Figures 2, 4 and 5, the dotted line curves are spectra yielded by reduced film thickness.

On the basis of the spectra presented in Figures 1 to 5, inclusive, the following general observations may be made:

Oxygenation alone, under the conditions described, yields a product, the infrared spectral characteristics of which are practically identical with those of the untreated polymer film. This holds consistently for all the polymer types examined, and indicates that no major structural change is effected by the oxygen treatment, even though continued for 24 hours.

Introduction of 50 p.p.m. of ozone into the oxygen stream effects several clearly defined changes in the polymer residue. Hydroxyl and carbonyl groups show a progressive increase, while olefinic structure, where present, exhibits a concomitant deterioration.

Of the elastomers studied, Butyl (GR-I) differs in two major respects on ozonization. The increase in hydroxyl content is relatively negligible, and the general decrease in transmittance at wave lengths above 7.0 microns, seen in common in the spectra of the other elastomers, does not develop. This would imply less structural modification of the Butyl polymer as a result of ozonization.

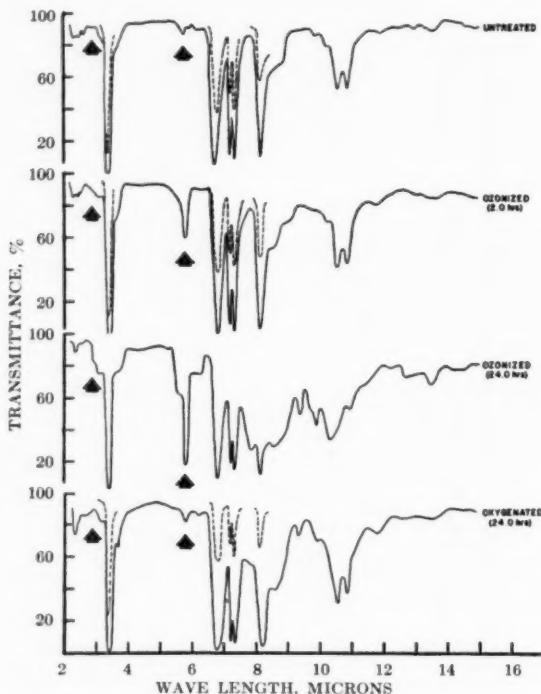


FIG. 5.—Relative effects of ozonization and oxygenation of 1 per cent solutions of Butyl rubber (GR-I) in *o*-dichlorobenzene.

It is interesting to note, in all the spectra, the absence of clearly defined bands in the 11- to 12-micron region which could be ascribed to hydroperoxides and epoxy linkages, in accordance with the work of Shreve, Heether, Knight, and Swern⁶. It may be assumed, therefore, that products of this type are not present in appreciable amounts in the films examined.

The spectral changes noted parallel somewhat those of Cole and Field⁶, who reported qualitative effects of air oxygenation at 100° C, and ultraviolet irradiation at 40° C, on specimens in the solid state, of various polymers and copolymers of isoprene, butadiene, and styrene.

In the present work, to estimate the quantitative extent of the variations

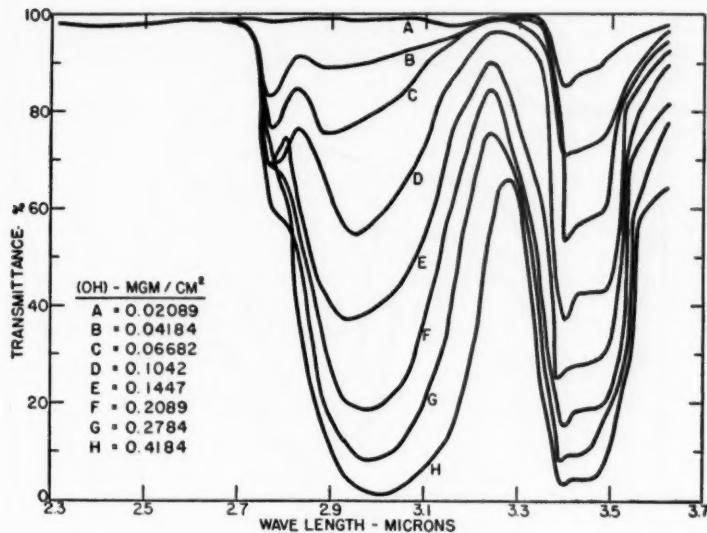
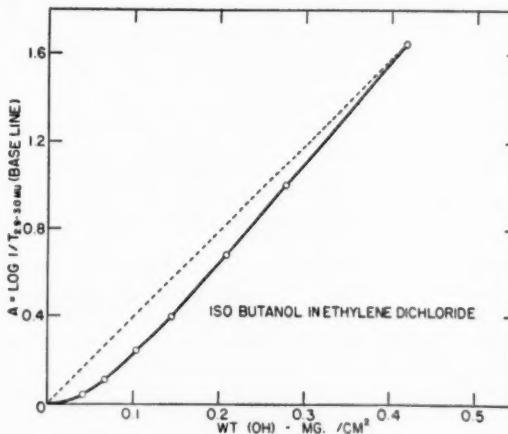


FIG. 6.—Isobutyl alcohol in ethylene dichloride.

observed in hydroxyl and carbonyl content, as a result of ozonization in solution at room temperature, the families of curves shown in Figures 6, 8, and 10 were obtained. In selecting the component pairs on which these curves are based, no attempt was made to simulate actual ozonization products. The deciding factors were functional group content and suitability for spectral study, from the standpoint of forming clear homogeneous solutions or films.

Variation of functional group concentration was obtained by preparing a series of solutions or mixtures of accurately weighed or measured proportions

FIG. 7.—Beer's law curve for hydroxyl. $2.9-\mu\text{m}$ band.

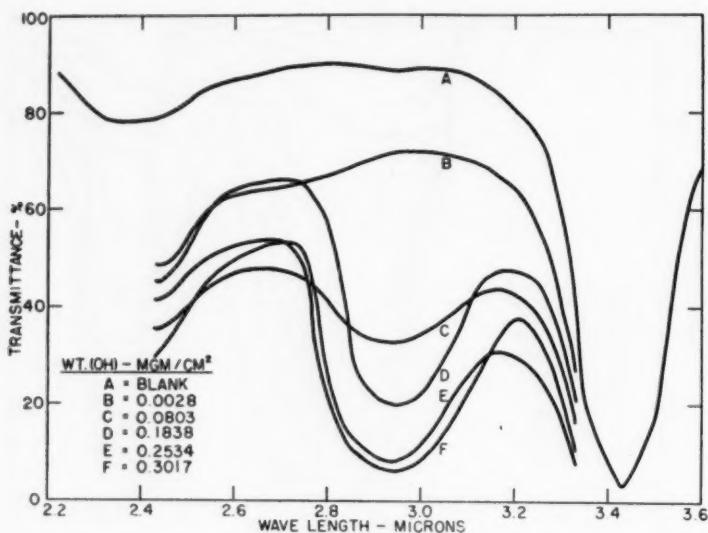
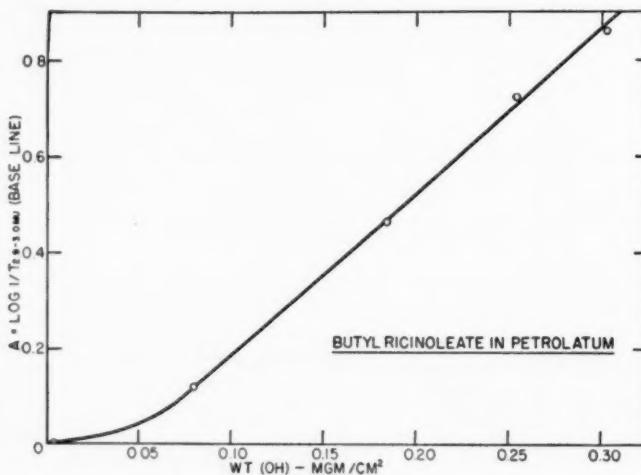


FIG. 8.—Butyl ricinoleate in petrodatum.

of parent compound to diluent. In Figure 6, the concentrations tabulated were computed from the known compositions of the respective solutions, and the cell thickness (0.03 mm.), of the single absorption cell used. In Figures 8 and 10, the concentrations shown were calculated from film weights and the supporting area of the rock salt plate, using the method of differential weighing, as described by Hunt, Wisherd, and Bohham.⁷

FIG. 9.—Beer's law curve for hydroxyl. 2.9- μ band.

In computing absorbance, as used in this paper, so called "base-line" transmittance values, obtained graphically from per cent transmittance curves, were employed. The base-line technique, as originally described by Wright⁸, facilitates the presentation of quantitative data by compensating for background variations and minor differences in film thickness, and by yielding analytical curves originating at zero.

In Figure 6, a displacement toward higher wave lengths with increasing isobutyl alcohol content is observed for the 2.9-micron band. This is verified by the relative constancy of the 3.4-micron C—H stretching band. In dilute solutions of isobutyl alcohol in ethylene dichloride, the relatively shallow band at about 2.77 microns may be considered as reflecting free or unassociated hydroxyl. At higher concentrations of the alcohol, hydrogen bonding occurs, causing a shift of the hydroxyl absorption peak toward 2.95 microns.

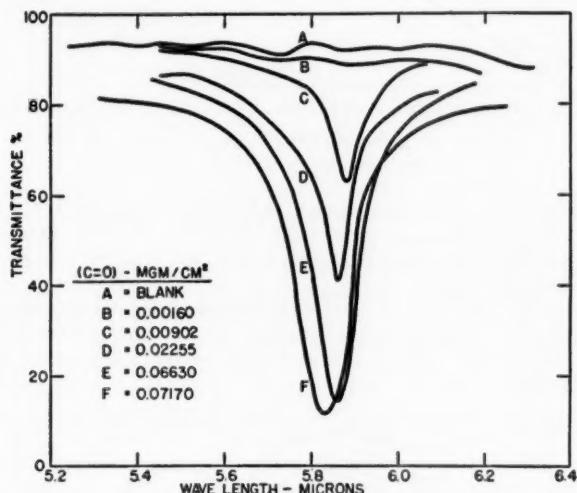
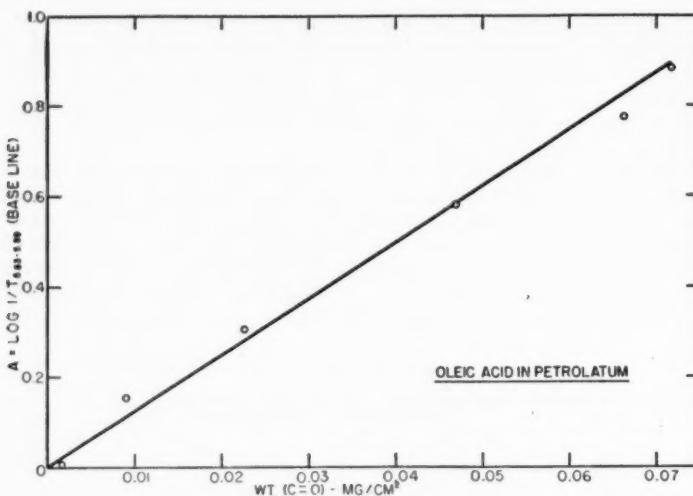


FIG. 10.—Oleic acid in petrolatum.

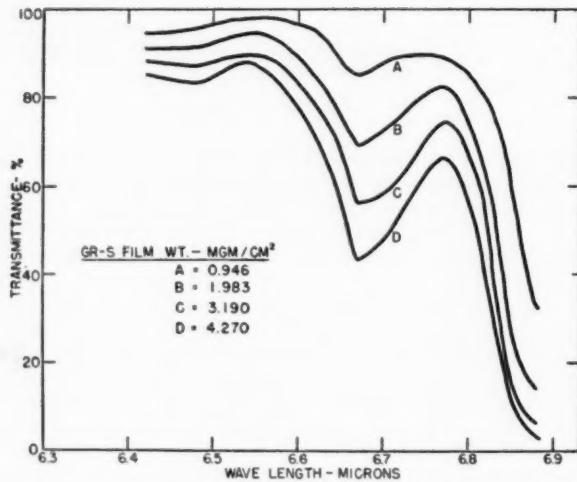
In Figure 7, the deviation from Beer's law caused by this shift is clearly seen. The dotted line represents a hypothetical curve for hydrogen-bonded hydroxyl, assuming that, at the highest isobutyl alcohol concentration shown, the hydroxyl groups are completely associated. The deviation from rectilinearity shown by the plotted data is a function of the ratio of free to hydrogen-bonded hydroxyl in this system.

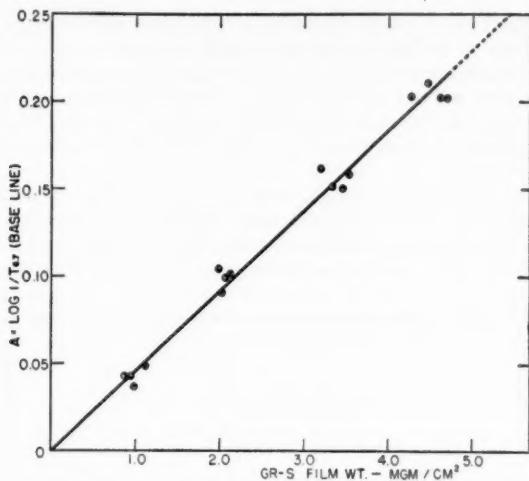
Figure 8 illustrates the variation in absorption due to hydroxyl concentration in a system differing widely from that of Figure 6. Here, the hydroxyl is attached to the central portion of a long-chain olefinic radical in an ester, contrasted to attachment to a four-carbon aliphatic radical. Nevertheless, the Beer's law curve of Figure 9 approximates that of Figure 7. The relationship between absorbance and the quantity of a functional group is apparently relatively independent of the structure of the remainder of the molecule to which the functional group is attached. Previous confirmation of this has been reported by Anderson and Seyfried⁹, who worked with petroleum hydrocarbons.

FIG. 11.—Beer's law curve for carbonyl. 5.8- μ band.

The interspersion of the shoulders at 2.7 and 3.2 microns in the curves of Figure 8 is due to deliberate, appreciable variations in film thickness. The rectilinearity of the major part of Figure 9 plot demonstrates the effectiveness of the base-line technique.

In Figure 10, the absorption maxima at 5.86 microns, due to carbonyl, show a tendency to shift to lower wave lengths with increasing concentrations of oleic acid. The plotted data of Figure 11 show substantially good agreement with a straight line.

FIG. 12.—GR-S film weight vs. adsorption at 6.67 μ .

FIG. 13.—Beer's law curve for GR-S film weight. 6.7- μ band.

The curves of Figures 7, 9, and 11 may be used to estimate percentage concentration of the respective functional groups in the ozonized polymers. The spectral data of Figures 1 to 5 are utilizable, provided the weights of the polymer films are known. These weights may be determined by direct weighing or by optical methods. Figures 12 and 13 illustrate an optical procedure for determining film weights of GR-S. The measurements are based on variations of absorbance at 6.7 microns. This band reflects the phenyl ring of the styrene component, and is apparently unaltered on ozonization. The sixteen points of Figure 13 are derived from four families of curves, in which is included that of Figure 12. It may be assumed from Figure 13 that, within reasonable limits, absorbance at 6.7 microns is a specific linear function of GR-S film weight.

Utilizing this optical method for determination of film weight, Figures 14 and 15 show the rate of accumulation, percentagewise, of hydroxyl and carbonyl groups in GR-S undergoing ozonization. Figure 14 indicates that hy-

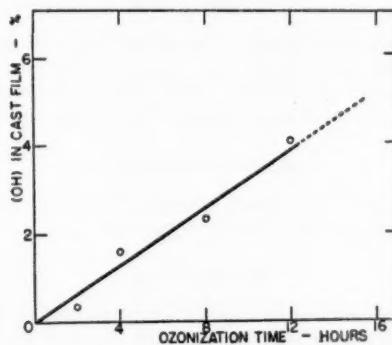


FIG. 14.—Percentage hydroxyl vs. ozonization time for GR-S gum.

droxyl accumulates at a relatively uniform rate, whereas in Figure 15 it is seen that the variation of carbonyl content is more complex.

Francis¹⁰ has shown that while the integrated intensity of the band at 5.8 microns, associated with C=O stretching, is relatively constant for compounds of the same type, an increase of as much as 70 per cent is observed in the integrated intensity of this band for esters, compared to the corresponding value for ketones.

This would indicate that the failure of the curve of Figure 15 to extrapolate through zero may be due to either a more rapid initial build up of carbonyl content or an initial preponderance of a structural environment of the C=O group different from that prevailing in the period from 2 to 16 hours of ozoniza-

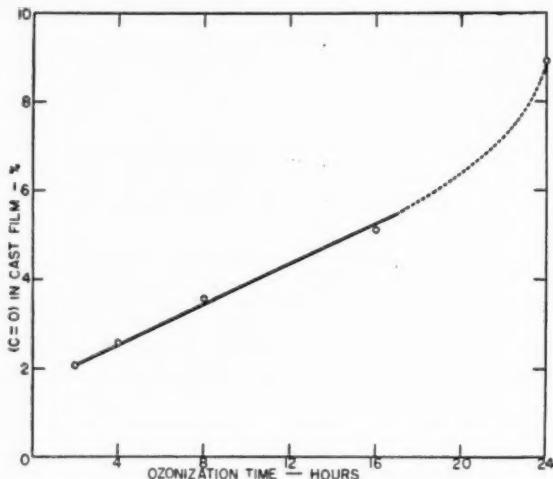


FIG. 15.—Percentage carbonyl *vs.* ozonization time for GR-S gum.

tion. Nevertheless, in the latter period a good approach to a straight-line variation is observed.

FUTURE WORK

This investigation is continuing. Curves similar to those of Figures 14 and 15 for GR-S are being obtained for the remaining crude polymers. It is intended to include vulcanizates of known formulation in this study, to determine the applicability of the procedures described to compounded and cured elastomer stocks.

ACKNOWLEDGMENT

The authors are indebted to Morris Alpert and Alvin D. Delman for valuable assistance in the experimental phases of this work.

SUMMARY

The work described consists of explorative studies with the ultimate objective of developing an accelerated ozone aging test for elastomers based primarily on compositional changes rather than on the conventional variation in

physical characteristics. Infrared spectrographic techniques were found to be admirably suited for the reflection of accumulation or depletion of specific structural linkages in polymer molecules undergoing ozonization. Purified gum specimens of Hevea, GR-S, nitrile rubber, Neoprene, and GR-I were dissolved in chlorinated hydrocarbon solvents such as ethylene dichloride or *o*-dichlorobenzene, and subjected to a stream of ozonized oxygen containing approximately 50 p.p.m. of ozone. Infrared spectrograms of films cast from the treated solutions show progressive intensification of clearly defined absorption bands at 2.9 and 5.8 μ , reflecting the functional groups hydroxyl and carbonyl, respectively. Methods for quantitating these changes by calibration against reference compounds are described. A means is available for following ozone degradation of polymers in terms of specific variations in molecular structure. Basic information of this nature is potentially useful in the development of an accelerated ozone aging test correlatable with aging under conditions of actual service.

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OZONE CRACK DEPTH ANALYSIS FOR RUBBER *

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In the past few years, much attention has been given to the weathering and ozone resistance of natural and synthetic elastomers. This has been due, in large part, to the advent of chemical rubbers in commercial manufacturing and acceptance of ozone as the component of natural weather which causes cracking of stretched rubber.

The synthetic elastomers, with apparently poorer weathering resistance than natural rubber, have presented rubber manufacturers with a serious problem of weather cracking, which has assumed greater proportions than with natural rubber. Confirmation of ozone as the agency that causes cracking of stretched rubber has provided the basis upon which accelerated tests for simulated weather cracking have been designed¹.

Being confronted with a serious problem and having a rapid, convenient method of testing, the rubber industry is searching for methods of controlling or preventing weather and ozone cracking. Much of the development work directed toward improving weather resistance uses ozone cracking as a guide. As a result, ozone testing and interpretation of results have become very important.

A major deterrent to the wider use of ozone testing and of natural weathering data is the lack of a satisfactory quantitative method of analyzing the test results. Quantitative data have many recognized advantages and appear to be a necessary requirement for exploratory development work in this field.

PRESENT METHODS

The present methods of data analysis can be divided into three groups indicative of the results they yield—judgment, indirect quantitative, and direct quantitative. Most of the methods in common use today are the judgment type, where the cracked sample is examined visually, and the rating is developed in the mind of the observer. In this group fall photographic ratings², ink impressions, and arbitrary visual ratings. The major disadvantage of this type of analysis is that it depends on the judgment and experience of the examiner for the values obtained; the conclusions may or may not be sound and the ratings may or may not be reproducible.

The indirect quantitative methods measure a known property of the exposed rubber and relate the change in that property to the extent of ozone cracking. An example of this type of test is measurement of modulus of the rubber after ozone exposure, which relates to reduction of cross-section due to ozone cracking and indirectly to the extent of cracking³. A similar test recently has been proposed which uses changes in electrical conductivity as the criterion. The objection to these types of test is that other influences concurrent with weathering or ozone attack may also affect the properties being measured.

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A direct quantitative method measures directly the changes wrought by ozone exposure. There have been few such methods proposed; an example is the measurement of the volume of ozone cracks by filling them with a heavy material, measuring the change in apparent specific gravity, and calculating the volume of the cracks from the difference in the apparent specific gravity. The results of this method are reproducible with difficulty because of the delicate handling required for accuracy.

Consequently, a search was made for a method that would yield direct quantitative results. The method should be easily performed, not require specialized equipment, be independent of human factors, and measure an important property in terms of ozone life. The development of the crack depth method of analysis is the result of this search.

THE METHOD

Crack depth is used as a measure of ozone and weather cracking results. This method is based on the premise that the growth of ozone cracks is inseparably bound to an increase in crack depth. Powell and Gough⁴ have shown that crack length and depth progress together, so that either would be an acceptable criterion; however, depth is more easily measured. Crack length is difficult to measure because in advanced stages of cracking the cracks grow together and lose their identity and personal judgment is required to identify each crack length. Crack depth is easily measured in cross-section, requiring no personal judgment in the determination of results.

Crack depth is measured by using a $20 \times$ microscope having a scale divided in millimeters, in the field. A relaxed longitudinal sectioned sample containing cracks is scanned, and the deepest cracks are measured, because they are the

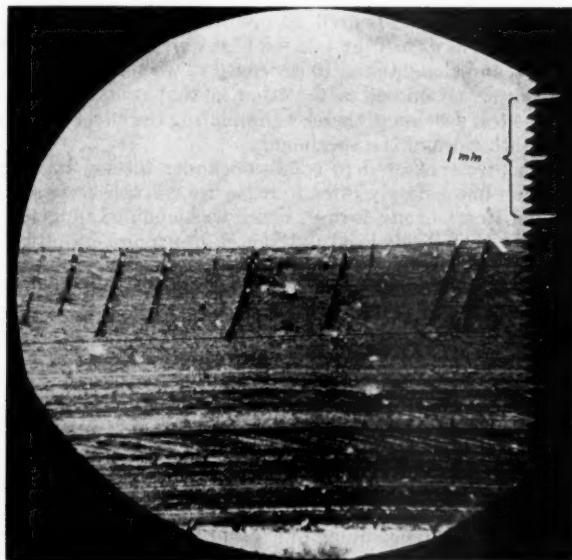


FIG. 1.—Sample as viewed for analysis.

active ones—the shallower cracks have ceased to have a directing influence on cracking⁴. The deepest crack and those within 10 per cent of the deepest are averaged to obtain the reported value. The data are reported as crack depth in millimeters. Reproducibility on replicate samples has been found to be ± 0.05 mm. with the equipment and test methods used.

Figure 1 shows a sample as viewed through the microscope. In Figure 1 the majority of the visible cracks are the same depth, varying less than 0.10 mm. There is no doubt in the viewer's mind which cracks are the indicative ones.

In order to demonstrate the usefulness of this crack depth method, it is used in the experiments that follow as a means of analyzing the results of ozone testing, in which some of the variables commonly associated with ozone testing are employed. Many of these variables have been reported in the literature previously, but have not had the benefit of quantitative data.

EXPERIMENTAL

Except as otherwise stated, the following procedure was used:

BASE FORMULATION

Natural rubber	100.00
Zinc oxide	5.00
Sulfur	2.75
Tetraethylthiuram disulfide	0.10
Benzothiazyl disulfide	1.00
Stearic acid	0.50
EPC black	55.00
	164.35

The formulation was press-cured 20 minutes at 280° F. in 4 \times 6 \times 0.10 inch sheets. Specimens measuring 1 \times 6 inches were cut from the plate, placed in tension clamps, and elongated to 10 per cent. Two specimens were mounted in each clamp, one superimposed on the other, so that cracking progressed from one surface in the test specimen, thereby eliminating the effect of relaxation due to cracking on both sides of the specimen.

The specimens were allowed to condition under tension in an absence of ozone for 24 hours immediately prior to exposure. Exposure was carried out in a Crabtree and Kemp ozone device⁵, which was modified to include a revolving sample basket that levels local differences in ozone concentration within the cabinet. The apparatus also contains a variable damper system for more precise control of ozone concentration. All tests were run at 70° to 80° F.

A check of ozone concentration by the potassium iodide decomposition method⁶ was made three times during each run. When the concentration was changed, concentration checks were made five times to be certain of stabilized ozone concentration. The time of exposure and ozone concentration were usually varied, and they are indicated in each experiment below.

Crack depth vs. exposure time.—Crack depth increased directly, but not proportionally, to exposure time, confirming previous work². The curve rises rapidly during the first few hours of exposure, after which it flattens and assumes a relatively constant slope. The change in slope may be explained by the hypothesis that, at the beginning of exposure, the ozone at the rubber surface is being constantly changed and is in close contact with the rubber, whereas when the cracks become deeper, the ozone at the depth of the crack is

changed less often and becomes exhausted, so that cracking is decelerated. Also, as cracking progresses, local relaxation occurs around the cracks, which probably contributes to a slackened rate of cracking.

Crack depth vs. ozone concentration and exposure time.—Ozone concentration and exposure time are both controlling factors in crack depth; therefore, knowl-

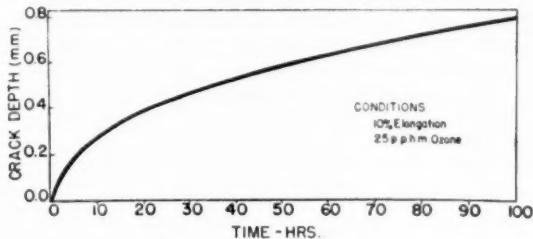


FIG. 2.—Crack depth *vs.* time.

edge of the interaction between the two would be helpful in designing experimental test conditions. The effect of variable exposure time and ozone concentration on crack depth is shown in a trifunctional graph in Figure 3.

Figure 3 shows that as ozone concentration is increased, the time to a given crack depth is markedly reduced. If 0.4 mm. is considered a crack depth at which significant cracking has occurred and the time *vs.* ozone concentration necessary to obtain that crack depth is plotted (Figure 8), it is evident that, in the range of 7 to 30 parts per hundred million ozone concentration, the time is reduced one-half as the ozone concentration doubles.

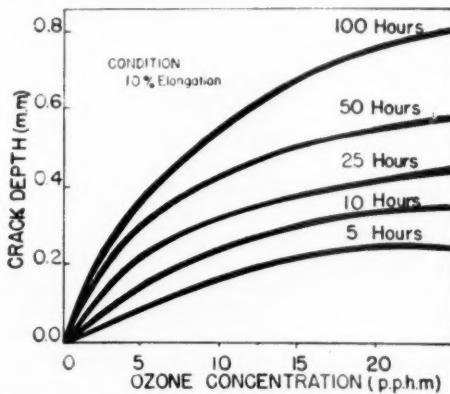


FIG. 3.—Crack depth *vs.* ozone concentration. Parts per hundred million at various exposure times.

Figure 3 also shows the crack depth to be expected under a wide variety of exposure conditions. This information is useful in determining ozone exposure conditions to approximate natural weather cracking when the depth of weather cracks is known under given conditions. The laboratory ozone conditions may be adjusted to a given crack depth in a variety of exposure periods, depending on the ozone concentration used.

Percentage elongation vs. crack depth.—In Figure 4 the importance of strain on the exposed samples can be seen. As the percentage elongation of the sample at the time of exposure increases, the crack depth decreases. This phenomenon has been explained by Powell and Gough⁴, who say in effect that the fewer cracks obtained at smaller elongations grow deeper, because the stress is concentrated at fewer points and less relaxation occurs from neighboring cracks.

This experiment was not designed to show a critical elongation where cracking is more severe, but to show the general trend. Separate samples were exposed in increments of 5 per cent from 5 to 50 per cent. This curve cannot be extrapolated to zero because there is a peak in the curve, the exact location of which is not known. The region between 0 and 5 per cent elongation is an interesting one in which to do further work.

Crack distribution.—It is generally well known that strain is necessary for ozone and weather cracking. Newton² and others pointed out that as cracks grow, local relaxation of strain occurs, so that some cracks grow more rapidly than others.

This condition is shown in the scale plot of Figure 5, showing crack location *vs.* crack depth.

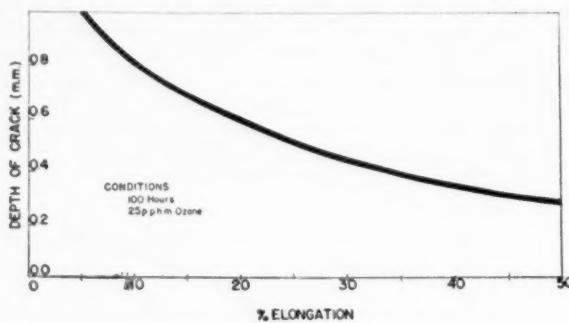
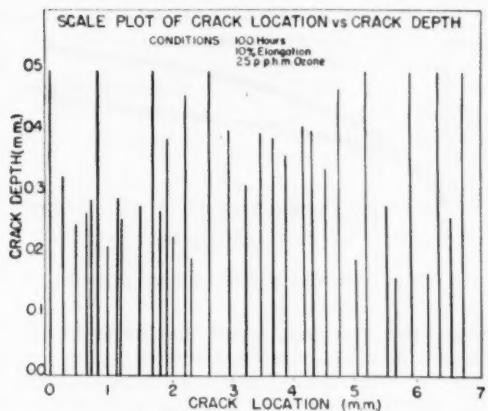


FIG. 4.—Elongation *vs.* depth of crack.

Figure 5 is a profile of cracks in a sample for a length of 7 mm. The length of each line in the figure represents the depth of an actual crack and its position on the horizontal coordinate indicates its position in the actual sample.

It is evident from an examination of Figure 5 that some of the cracks have grown much more rapidly than others. After 100 hours' exposure, used in this test, there were 35 cracks visible, of which only 13, or 37 per cent, had grown to a depth of 0.4 to 0.5 mm. If the sample had been examined under higher magnification, it is possible that many small cracks would have been observed and thus the percentage of cracks which had grown to appreciable crack depth would be further reduced. This finding, that only a small percentage of the cracks originated in a sample on exposure to ozone grow to any great depth, is in agreement with the earlier work of Powell and Gough⁴.

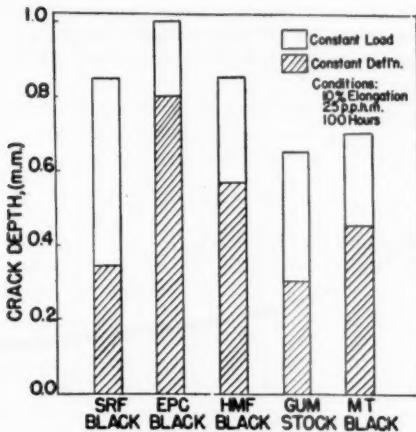
In the method proposed here for evaluating the results of ozone exposure, only those cracks which have reached the greatest depth are being considered. In all the experiments reported here, there were always a number of cracks in each sample which were nearly equal in crack depth and considerably deeper than all the other cracks in the specimen.

FIG. 5.—Scale plot of crack location *vs.* crack depth.

Constant load vs. constant deflection.—Samples measuring 1 \times 6 inches were cut from a single molded plate. One set of samples was placed in a fixture which clamped one end of the piece rigidly. The other end of the sample was free. A small metal container was attached to the free end of the sample and sufficient lead dust was placed in the container to stretch the sample 10 per cent. This method of preparation was compared with a method in which a sample was stretched 10 per cent and clamped in that position.

The sample under constant load exhibited creep and, at the end of the exposure time, showed greater extension than the sample held at constant deflection.

Figure 6 shows the crack depth obtained by using the two methods on stocks containing equal volume loadings of different carbon blacks. Constant-load

FIG. 6.—Constant load *vs.* constant deflection.

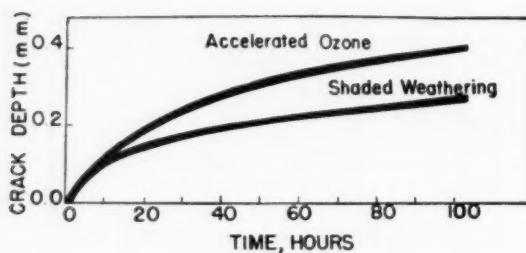


FIG. 7.—Correlation of ozone and actual weathering.

application during exposure is more severe than constant deflection, as shown by deeper cracking. However, the same general trends apply, regardless of which method is used. As cracking progresses under constant load, the local stress around the cracks increases as a result of reduction in cross-section. Using the constant-load method, the effect of stress relaxation is avoided, and cracking proceeds more rapidly to a more severe end-point. The constant-load method of sample exposure has been proposed as a more sensitive method for ozone exposure⁸.

Most commercial rubber products operate under constant deflection in the areas exposed to ozone or weather. Stress relaxation plays an important part in ozone resistance of most products, and the beneficial effects of this condition should not be eliminated by the method used.

CORRELATION OF WEATHER AND ACCELERATED OZONE TESTING

An experiment was made to determine the correlation between exposure in an ozone chamber and actual weathering.

Figure 7 shows that ozone cracking and actual weather exposure, as measured by the crack-depth method, are related. The shapes of the curves are very similar, but the values of crack depth are different because of the differences in ozone concentration in contact with the samples. It was shown previously that in the areas of low ozone concentration, a small change in ozone concentration makes a large change in the crack depth. As a result, the difference between

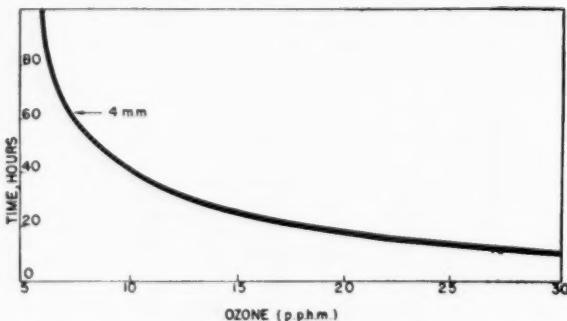


FIG. 8.—Time and ozone concentration required to produce ozone cracking equivalent to actual weathering for 3 weeks' exposure.

actual weathering and laboratory ozone exposure was marked. At the time of weather exposure, the average atmospheric ozone content was 3.5 parts per hundred million of air. This lower ozone concentration has resulted in reduced weather cracking when compared to the results obtained in the ozone chamber, where the concentration was 5.03 parts per hundred million of air.

In order to show a correlation, the samples exposed to sunlight must not be compared to ozone-exposed samples. Sunlight exposure exerts a protective influence on weather-exposed samples which is not present in laboratory ozone tests. Shaded weather-exposed samples show a correlation with accelerated ozone tests. Exposure temperature must be taken into account when attempting to correlate accelerated exposure with service exposure⁷.

The correlation of the laboratory method with actual service conditions is a great asset in reducing experimental findings to practice. A correlation exists between ozone crack depth produced in the laboratory and weather crack depth produced under natural weather conditions. Figure 8 shows a constant crack-depth curve for a range of time and ozone concentration. The crack-depth curve is for 0.4 mm., which is the depth obtained on the same stock exposed to natural weather for 3 weeks. This curve has proved valuable in determining laboratory ozone exposure conditions necessary to duplicate weather exposure conditions.

SUMMARY

The factors that control weathering and ozone resistance are not fully understood. A major deterrent to a better understanding of these factors is the lack of a satisfactory quantitative method of analyzing the results of ozone and weathering tests. A method has been developed which follows the change in crack depth as the criterion of the extent of damage that has taken place. It has been shown that, when crack growth takes place, the depth increases proportionally. The depth of the crack is measured with the 20 X microscope in a cross-section made normal to the length of the cracks. The major cracks, which have the directing influence on the extent of cracking, are the deepest ones, and are all nearly the same length. This method has been used to analyze results of ozone cracking in which commonly recognized variables were employed. The results confirm some previously reported trends with quantitative data. This method can be used in measuring the effect of compounding variables, where results are desired in terms of a dimension of actual ozone cracking. This method is performed with moderate ease, does not require specialized equipment, is independent of human judgment, and is directly related to the growth of ozone cracks. It should contribute to a better understanding of the factors that control weathering and ozone resistance of natural rubber and other elastomers.

ACKNOWLEDGMENT

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OZONE RESISTANCE OF NEOPRENE VULCANIZATES

EFFECT OF COMPOUNDING INGREDIENTS *

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In recent years interest in the deteriorating effect of ozone on elastomer vulcanizates has increased. This has been, in part, due to the more extensive use of elastomeric materials in already established applications and, to the need in part, for resilient articles in newly developed services where ozone deterioration is known to be very severe. The development and increased use of synthetic elastomers having ozone-resistant properties differing from those of natural rubber also has contributed to the increased interest in this field of investigation.

Two examples of applications in which attack by ozone limits service life are the use of products under conditions of exposure to the weather and their use in proximity to high-voltage discharges. Although ozone is only one of several agents influencing deterioration of elastomeric products on outdoor exposure, it frequently proves to be the most severe. High concentrations of ozone produced by electrical discharges deteriorate most elastomeric products so rapidly as to impair their service life seriously.

The estimated service life of vulcanizates subject to ozone exposure is frequently based on accelerated tests in artificially produced ozonized air or oxygen at concentrations considerably higher than will be experienced in service. As in the case of other accelerated aging tests, the significance of the results relative to actual service life lessens as the difference between test and service conditions becomes greater. Nevertheless, the rubber technologist frequently is called upon to produce vulcanizates which will resist attack by ozone at abnormally high concentrations in order to meet test requirements which have been established as a quality control for products subject to ozone attack in service. The purpose of this paper is to report the effects of compounding on the resistance of Neoprene vulcanizates to attack by ozone when subject to such accelerated tests.

Different elastomers vary greatly in their basic resistance to ozone attack. Neoprene obtained early recognition as a material markedly superior in this respect¹. The resistance of Neoprene vulcanizates to deterioration by atmospheric ozone during outdoor weathering is particularly outstanding². The type of surface cracking attributable to ozone attack, which so often results in the failure of less resistant elastomers exposed to weathering, does not appear on properly compounded Neoprene vulcanizates even after long outdoor exposure. For this reason Neoprene is used extensively in products designed for outdoor service.

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Conventional Neoprene vulcanizates crack, however, when exposed to concentrations of ozone significantly higher than those encountered during outdoor weathering. As would be expected, their resistance to attack at these concentrations is markedly superior to that of elastomers which are subject to cracking on weather exposure. Figure 1 shows the comparative effects of ozone on vulcanizates of a number of commercially available elastomers. These compounds all contained 30 volumes of SRF carbon black per 100 volumes of elastomer. No waxes were included, and approximately the same amount of antioxidant was present. The specimens were subjected to 25 per cent strain and exposed for 8 hours to ozone at a temperature of $24^\circ \pm 1^\circ \text{ C}$, and at a concentration of 1 to 3 parts per million. The elastomers tested fell into two classes with respect to ozone resistance. Those which may be classified as ozone resistant are the general-purpose Neoprenes: GR-I, Thiokol, and Hycar PA-21. GR-S, low-temperature GR-S, Buna-N, natural rubber, and Neoprene Type FR must be classified as less ozone-resistant.

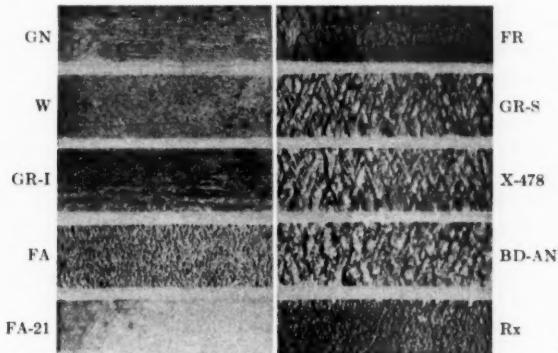


FIG. 1.—Effect of ozone on different elastomers.

GN. Neoprene Type GN

FR. Neoprene Type FR

W. Neoprene Type W

GR-S. Standard GR-S

GR-I. Butyl

X-478. GR-S X-478

FA. Thiokol Type FA

BD-AN. Buna N

FA-21. Hycar PA-21

Rx. Natural rubber

The Neoprene samples shown, which have resisted attack by ozone under these conditions of exposure, crack, even to the point of breaking, at higher concentrations of ozone or on longer exposure at the same concentration. On the other hand, these compounds have been exposed outdoors for as long as three years and similar compounds up to eleven years without any visible sign of the type of cracking generally associated with ozone attack. This observation emphasizes the need for careful interpretation of data obtained from accelerated ozone tests when applied to the estimation of outdoor service life under normal atmospheric conditions.

FACTORS AFFECTING SELECTION OF TEST METHODS

The effect of ozone on elastomers is influenced by a great many variables which must be considered before an investigation of compounding is undertaken. Some of these variables are so important that slight changes in conditions of exposure alter drastically the results obtained. It is generally rec-

ognized that cracking as a result of ozone exposure takes place only if the vulcanizate is under tension. Several investigators³ have shown that the degree of tension affects the degree and type of cracking. With certain vulcanizates, notably those of rubber and the butadiene-containing elastomers, a so-called critical strain or critical stress has been observed, above and below which ozone cracking is less severe.

Neoprene vulcanizates, on the other hand, become more susceptible to ozone attack as stress and strain are increased. No intermediate critical range has been reported. It has been observed that Neoprene vulcanizates must be subjected to both stress and strain of an appreciable degree before they crack under the influence of ozone. For example, a test-specimen elongated and allowed to relax will not crack though it is still strained. Neither will a stock highly loaded with filler crack if stressed insufficiently to place it under a significant strain, even though the stress may be substantial.

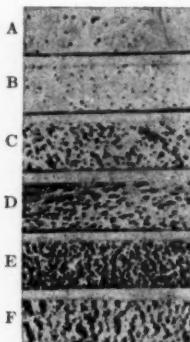


FIG. 2.—Effect of conditioning.

- A. 2 minutes
- B. 30 minutes
- C. 2 hours
- D. 4 hours
- E. 24 hours
- F. 72 hours

Because of these marked effects of stress and strain on ozone resistance, the stress relaxation and modulus characteristics of a specimen can effect radical variation of results, depending on the test procedure. This is demonstrated by the effects of conditioning stretched samples for various periods of time prior to exposure in ozone. Figure 2 shows the results of ozone attack on a Neoprene Type GN vulcanizate containing 40 volumes of EPC carbon black per 100 volumes of Neoprene. The specimens were elongated 25 per cent and allowed to rest for different time intervals prior to exposure. It is obvious that the longer the conditioning period the better the resistance to cracking. This is attributed to stress relaxation. A gum Neoprene Type GN vulcanizate and ones containing 40 volumes of hard clay and 40 volumes of MT carbon black were tested, using the same conditioning periods. The clay stock, like the EPC carbon black stock previously tested, was known to possess high tension set. It also improved in ozone resistance as the time between stretching and exposure to ozone was increased. The MT carbon black-loaded stock and the

gum stock, which were known to have low tension set, were less affected by conditioning.

The ozone concentration and the duration of exposure are variables which obviously affect the severity of ozone testing and need no further discussion. Continuity or discontinuity of testing is another important variable. Stress relaxation, as in the case of variation of conditioning period prior to exposure, affects the results if ozone tests are interrupted.

The temperature at which testing is conducted affects the severity as well as the type of cracking⁴. Increasing the temperature accelerates the rate of cracking, with the development of more but smaller cracks.

If the supply of ozone introduced into the test chamber is small relative to the number, susceptibility, and size of test-specimens, it leads to inconsistent results. Because ozone combines with the elastomer, the presence of a large number of samples highly susceptible to ozone attack results in lower effective ozone concentration than would be present if the samples were fewer in number or more resistant to ozone attack. This variation becomes most important when testing under conditions of limited ozone supply. In like manner, other organic matter, such as wood and paper, which reduce ozone to oxygen, lowers the concentration. For this reason, all cellulosic material used in an ozone test unit should be coated with wax or spar varnish.

Variations in sample preparation also are known to affect ozone test results. Strains induced prior to or during vulcanization⁵, imperfections resulting from flow cracks, porosity, foreign matter, poor dispersion, etc., and surface oxidation are variables which must be controlled in order to obtain reproducible results.

PREPARATION OF TEST SPECIMENS

Because this investigation did not include a detailed study of variables other than compounding ingredients, testing was restricted to an established procedure. All compounds were mill-mixed. Where several ingredients were tested in a common base formula, masterbatches of the base stock were mixed on a 30-inch mill, and the individual batches were prepared by adding the ingredients to be tested on a 12-inch mill. To minimize grain effect, the stocks were carefully sheeted off the mill at 0.08- to 0.09-inch gauge thickness. The uncured sheets were stored on stainless steel trays in a dust free cabinet for 24 hours at room temperature before curing. Except where otherwise noted, all Neoprene compounds were press cured for 20 minutes at 153° C, in the form of laboratory test sheets 0.075 ± 0.003 inch thick. In the case of compounds designed to investigate ingredients, such as antioxidants, which are known to be effective in small amounts, precautions were taken to avoid contamination of one stock by another. Sheets were cured between cellophane to avoid transfer of the variable ingredient from one sheet to another through contamination of the mold surface and, after curing, all sheets were separated from each other by paper and stored in the dark until tested.

For testing at constant strain, samples were prepared by die-cutting strips $\frac{1}{4}$ inch wide. These specimens were mounted on a spar-varnished wooden frame having parallel members separated 3 inches by means of dowels. The specimens were attached at $\frac{1}{2}$ -inch intervals and, except where noted otherwise, were elongated 25 per cent. The area surrounding the point where the sample was attached to the frame was frequently under a higher strain than the rest of the sample. Therefore the ends were coated with molten microcrystalline wax, to prevent premature breakage in this area. In all cases twenty-four specimens

were mounted on each rack. After elongation of the last specimen, 30 minutes were allowed to elapse before exposure to ozone. Figure 3 shows the assembly prior to ozone exposure. Photographs were taken at time intervals during the test to provide a record of the progress of cracking. General appearance based on the frequency and depth of cracks was selected as a basis for rating ozone resistance. For record purposes a numerical rating system of from 0 (no cracks) to 10 (broken) was applied. Figure 4, showing samples considered

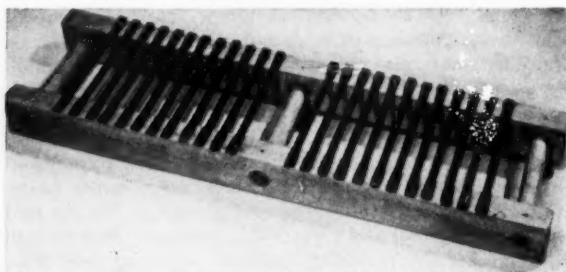


FIG. 3.—Assembly for testing at constant strain.

representative of each digit, was used as a reference guide. The sample marked 4 was judged to represent a more advanced stage of ozone attack than sample 3 because the cracks are much deeper. The same comparison influenced the evaluation of samples 6 and 7. This effect does not photograph well, and the subheadings in the figure under the term "size" are an attempt to explain it in words.

For testing under constant load T-50 dumbbells were used⁶ (ASTM D 599-40T). The assembly, as shown in Figure 5, consisted of a spar-varnished

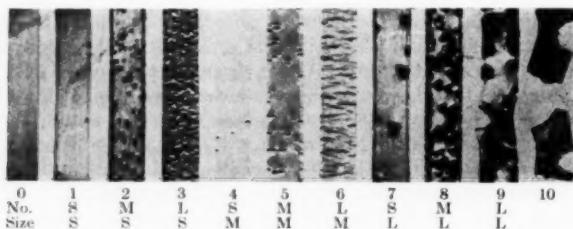


FIG. 4.—Rating system for ozone cracking.

S = small
L = large
M = medium

wooden support to which the samples were attached. Lead weights were clamped to the dumbbells giving a load of 100 pounds per square inch. A protective film of petrolatum was applied around the shoulder of the dumbbell, because otherwise a concentration of stresses at this point gave premature breaks during testing. Time to breakage was selected as the measure of ozone resistance. Good correlation in all cases was not obtained between the results of constant strain and constant load testing. This in part may be attributed

to the influence which tear resistance had on the breaking time measured in the constant load method.

TEST CHAMBERS

Two test units were used in this investigation. One unit consisted of a cubical chamber, 2 feet on each side, constructed of stainless steel except for a transparent Lucite front for viewing the specimens, and a top-opening plywood lid well saturated with paraffin wax. Ozone was supplied to the chamber by a current of air dried over calcium chloride which was passed at a rate of approximately $\frac{1}{4}$ of a cubic foot per minute over a generating unit consisting of two $\frac{1}{16}$ -inch thick perforated aluminum plates approximately 5 square inches in

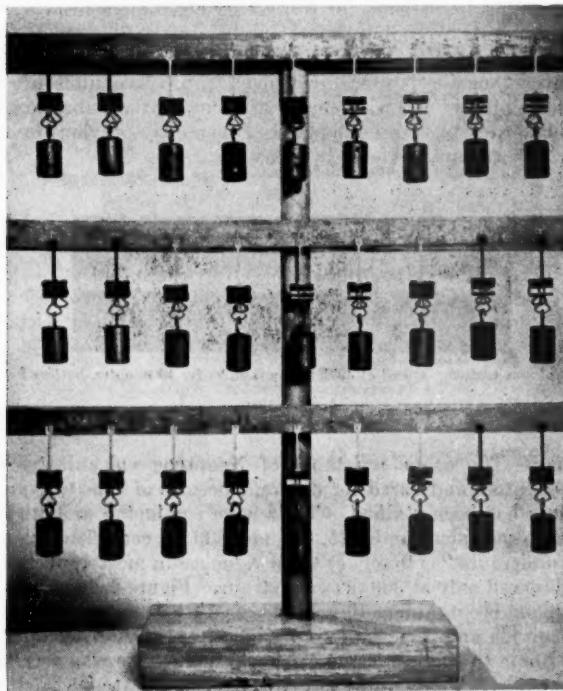


FIG. 5.—Assembly for testing of constant load.

metallic area separated by a 0.012-inch thick mica sheet. A transformer was used to supply 1700 volts between the plates. Uniform distribution of ozone in the chamber was assured by means of an electric fan with 5-inch blades. The apparatus was operated at a controlled ambient temperature of $24^\circ \pm 1^\circ$ C. Ozone concentration varied between 1 and 3 p.p.m. as determined by the Crabtree and Kemp method². Samples were limited to a maximum of six frames (Figure 3) under test at one time. All of the specimens for any given set of compounding variables were exposed at one time. Tests conducted in this apparatus are referred to throughout this paper as having been carried out at the low ozone concentration.

Because many Neoprene compounds do not crack after unduly long periods of exposure at ozone concentrations of 1 to 3 p.p.m., it was necessary to run tests in a much higher concentration to determine differences among the more ozone-resistant specimens. An apparatus similar to that described in American Society for Testing Materials Test Method Designation 470-46T was used and test-specimens were exposed to ozone at a concentration of 100 p.p.m.⁷. Subsequently in this paper, tests so conducted are referred to as having been carried out at the high ozone concentration.

EFFECT OF COMPOUNDING INGREDIENTS

Waxes.—Waxes are the most generally recognized and extensively investigated compounding ingredients for protecting elastomers from ozone attack. If present in amounts exceeding their solubility in the elastomer, they bloom, forming a protective surface film inert to ozone. If not disturbed, wax films efficiently protect against ozone. However, protective films are easily destroyed by flexing, rapid and wide changes in temperature, abrasion, and washing. The subject having been adequately covered by previous investigators⁸, a study of waxes was not included in this work.

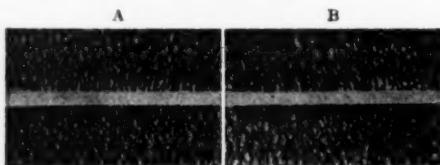


FIG. 6.—Effect of acceleration. Cured at 307° F; top samples for 10 minutes, bottom for 20 minutes.

A. Permalux
B. Thionex

Accelerators.—The ozone resistance of Neoprene vulcanizates containing different accelerators and cured for different periods of time to give a range of modulus values has been studied. Tests were conducted at both ozone concentrations with specimens under 25, 100, and 300 per cent elongation. Except for stocks so undercured as to render them valueless in most applications, differences were observed only at 300 per cent strain. Figure 6 shows two Neoprene Type W compounds containing 40 volumes of MT carbon black and cured with 4 parts of magnesia and 5 parts of zinc oxide after exposure under 25 per cent strain for 30 hours to the low ozone concentration. One was accelerated with one part of the di-*o*-tolylguanidine salt of dicatechol borate (Permalux) and the other with 1 part of tetramethylthiuram monosulfide (Thionex). One part of sulfur was included in the latter compound. Cures of 10 and 20 minutes at 153° C are shown. Under these test conditions no differences in ozone resistance were apparent. The stress in these samples at 25 per cent elongation varied from 85 to 119 pounds per square inch as determined on the Instron universal testing machine. Even when tested at 100 per cent elongation, at which the stress values varied from 180 to 380 pounds per square inch, no effect on ozone resistance was observed. At 300 per cent elongation, however, the stress varied from 1150 to 2275 pounds per square inch, and the lower modulus stocks were more ozone resistant.

In addition to the compounds shown, Neoprene Type W vulcanizates accelerated with 2-mercaptoimidazoline (NA-22), 0.5 and 1 part, and salicylic

acid (Retarder W), 1 part, cured for 10, 15, and 20 minutes at 153° C were compared. Neoprene Type GN compounds similarly cured containing NA-22, 0.5 and 1 part, Permalux, 1 part, antimony trisulfide, 1 part, as well as an unaccelerated stock, also were compared. Results were similar to those observed with the accelerators previously studied. Because in the great majority of ap-

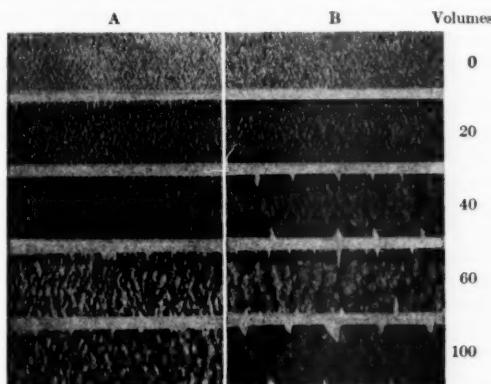


FIG. 7.—Effect of loading.

- A. FT carbon black
- B. Hard clay

plications Neoprene compounds must be relatively well cured and strains seldom exceed 100 per cent, variation of modulus by adjustment of accelerators and curing conditions does not, therefore, constitute an effective method for controlling ozone resistance.

Fillers.—The amount and type of fillers used in a Neoprene vulcanizate have a pronounced effect on ozone resistance. In general, with a given filler, increasing the loading decreases resistance to ozone attack. Figure 7 shows the

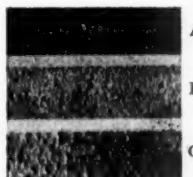


FIG. 8.—Comparison of fillers at 40-volume loading.

- A. FT carbon black
- B. Hard clay
- C. Natural whiting

effect on Neoprene vulcanizates, containing varying loadings of FT carbon black and clay, of exposure at 25 per cent strain to the low ozone concentration for 24 hours. A gum stock as well as stocks loaded with 20, 40, 60, and 100 volumes of filler are compared. Not only does increased loading with both fillers decrease the ozone resistance, but the clay-loaded compounds are less resistant than the FT carbon black-loaded compounds.

The use of coarse particle-sized fillers, such as natural ground whiting, as loading in Neoprene is known to affect outdoor weathering adversely, although the type of attack generally attributed to ozone is not apparent under these conditions. It also is interesting to note that such fillers have a very adverse effect on ozone resistance. Figure 8 shows the results obtained when Neoprene vulcanizates containing 40 volumes of FT carbon black, clay, and natural whiting, respectively, are exposed at 25 per cent strain for 12 hours at the low ozone concentration. Ozone resistance of the stock containing whiting is obviously very poor in comparison with that of the stocks containing the finer particle-sized materials.

In addition to the samples shown in Figures 7 and 8, other Neoprene vulcanizates containing a number of different amounts and types of loading, including blends of two fillers at different ratios, were tested both at constant strain and under constant load. Results of all tests are summarized in Table I. It is clear that the adverse effect of loading on ozone resistance is not attributable solely to increased stress during exposure. Results of test conducted under a constant load of 100 pounds per square inch in general follow the same pattern as those conducted at constant strain. Extremely heavily loaded compounds constitute an exception. In these cases, however, it was observed that the load of 100 pounds per square inch imposed was insufficient to produce any measurable deflection. It also is observed that among the different fillers, there is no correlation between modulus (shown in the table as stress at 300 pounds per square inch) and ozone resistance. It therefore is concluded that the adverse effects of increased amounts and particle sizes of loading material on ozone resistance are independent of their effects on the stress-strain characteristics of the vulcanizate.

Plasticizers, Softeners, Extenders, and Tackifiers.—Liquid plasticizers vary greatly in their effect on the ozone resistance of Neoprene vulcanizates. In general, the petroleum base types produce a slight though measurable impairment. A number of commercially available types were tested in a Neoprene compound containing 40 volumes of MT carbon black and 20 volumes of the oil per 100 volumes of Neoprene. Except for one brand, known to contain incompatible fractions, which bloomed forming a protective surface film, all were found to produce slightly less ozone-resistant vulcanizates than the control containing no oil. The effects of commonly used process oils are so slight, however, that they may be used at least up to the amount tested in most Neoprene compounds without concern as to their effect on the ozone resistance.

Several esters and a number of other types of plasticizers commonly used in compounding Neoprene for low-temperature performance were tested in the same manner as the petroleum oils. Results are shown in Table II for tests conducted under constant strain at the two ozone concentrations and for tests under constant load at the low ozone concentration. Although there is poor correlation between the constant strain and constant load data, it is evident that, in general, the use of ester type plasticizers significantly reduces the ozone resistance of Neoprene vulcanizates.

Some oils from vegetable and animal sources have been found to enhance the ozone resistance of Neoprene. Notable among these in decreasing order of superiority are linseed, tung, castor, menhaden, soybean, cottonseed, and corn oil. Peanut oil give no improvement over the control containing no oil. Coconut oil has a serious adverse effect which may indicate that the degree of unsaturation of these oils has a bearing on their ozone resisting characteristics.

TABLE I
EFFECT OF FILLERS ON OZONE RESISTANCE OF NEOPRENE VULCANIZATES

Base formula					
	Neoprene Type GN	100			
	Stearic acid	0.5			
	Magnesia	4			
	Zinc oxide	5			
	Filler	As shown			
	Light process oil	Approx. 10% wt. of filler			
Type of test			Constant strain, High		Constant load Low
Ozone concentration			(30 min.)		
Exposure time					
	Neoprene by volume (%)	Stress at 300% elonga- tion (lb./sq. inch)	Rating	Hours to failure	
None	97	300	1	>20.0	
MT carbon black	75	800	2	13.5	
	60	1575	3	10.5	
	50	2000	4	8.0	
	40	—	6	9.0	
FT carbon black	75	650	1	13.8	
	60	1150	1½	10.5	
	50	1375	2	9.0	
	40	1375	6	15.0	
SRF carbon black	75	1900	1	14.3	
	60	—	3	13.0	
	50	—	Broke in stretching	11.0	
MAF carbon black	75	2200	1	16.2	
HAF carbon black	75	2500	1	19.0	
EPC carbon black	75	2000	1	18.8	
Hard clay	75	800	1½	13.0	
	60	1125	3	12.0	
	50	—	10	17.0	
	40	—	Broke in stretching	>20.0	
Natural whiting	75	225	2	4.0	
	60	200	10	3.0	
	50	225	10	2.5	
	40	450	Broke in stretching	2.75	
Natural whiting/clay, 50/50	75	550	1½		
	60	600	6		
	50	675	10		
	40	825	10		
Natural whiting/clay, 75/25	75	850	1		
	60	975	3		
	50	1075	8		
	40	—	10		
Hard clay A	60	850	3		
B	60	750	3		
C	60	1125	3		
Coated precipitated calcium carbonate	60	525	1	10.5	
Barytes	60	250	10		
Calcium silicate	60	950	10		
Asbestene	60	775	3		
Magnesium carbonate	60	950	3		

TABLE II
EFFECT OF LIQUID PLASTICIZERS

Type of test Ozone concentration Exposure time	Constant strain		Constant load Low Hours to failure
	High (30 min.) Rating	Low 7 Hours Rating	
None	4	2	>24
Dibutyl phthalate	6	3	9.5
Diocetyl phthalate	5	3	11.4
Diallyl phthalate	7	2	14.2
Dicapryl phthalate	6	2½	10.7
Triresyl phosphate	6	2½	12.2
Tributoxyethyl phosphate	8	1½	15.3
Dibutyl sebacate	6	4	7.6
Diocetyl sebacate	6	3	12.8
TP-90-B ^a	7	3	6.9
Plasticizer SC ^b	6	3	7.2
Flexol 3GO ^c	6	3	7.6
Flexol TOF ^c	5	2	12.4
Arneel TOD ^d	6	3	18.2

^a Supplied by Thiokol Corp.

^b Supplied by E. F. Drew & Co.

^c Supplied by Carbide & Carbon Chemicals Corp.

^d Supplied by Armour & Co.

Figure 9 shows a comparison of several vulcanizates containing different vegetable oils after exposure at 25 per cent strain for 17 hours to the low ozone concentration. Esters derived from castor oil were investigated. Methyl-, butyl-, benzyl-, and butylacetyl ricinoleates give the same approximate ozone resistance as castor oil. Methylacetyl ricinoleate gives less resistance, and a processed type of castor oil is relatively ineffective. All compounds tested contained 40 volumes of MT carbon black and 20 volumes of oil per 100 volumes of Neoprene.

Several commonly used softeners, extenders, and tackifiers were tested using the same amount and same base formula just described. Factices including white, amber, and brown varieties derived from soybean, rapeseed, and castor

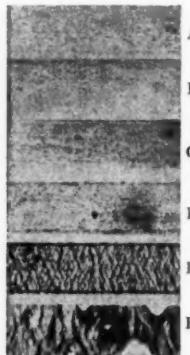


FIG. 9.—Effect of vegetable oil.

- A. Linseed
- B. Tung
- C. Castor
- D. Cottonseed
- E. Control
- F. Coconut

oils; mineral rubber; coumaroneindene resins of different melting points, and butadiene-styrene resins were tested. Little if any effects on ozone resistance were noted. This type of material is commonly used in compounding elastomers for ozone resistance. They are known to produce vulcanizates having a high degree of stress relaxation. The test procedure used in this investigation permitted only 30 minutes' time to elapse between stretching the samples and exposure to ozone. This was apparently too short a period to allow a significant degree of relaxation to occur. It is concluded, therefore, that if materials of this type provide ozone resistance, it only results from the stress relaxation they produce in the vulcanizate.

Unlike the other ingredients of this type, wood rosin provided a degree of resistance to ozone sufficient to warrant its selection in preference to the other materials.

Antioxidants.—A number of antioxidants known to protect Neoprene vulcanizates effectively against deterioration by oxidation as measured by oxygen pressure or oven-aging tests were evaluated for their effects on ozone resistance. Some were found to provide excellent protection from attack by ozone, especially in the case of compounds designed for dynamic service where protective wax film is destroyed and where vulcanizates having high permanent set may not be used. Others showed only moderate ozone resistance, and some even had a deleterious effect. The concentration of ozone during exposure and the amount of antioxidant used had a pronounced bearing on the relative efficiency of the different antioxidants on ozone resistance. For this reason, conclusions pertaining to comparative effectiveness under one set of conditions will be misleading if applied to another set of conditions.

COMPARISON OF VARIOUS ANTIOXIDANTS

Antioxidants were compared first in gum stocks. One per cent of antioxidant was used, based on the Neoprene, and vulcanizates were exposed to ozone at high concentration, 100 p.p.m., and at low concentration, 1 to 3 p.p.m. Tests at the high concentration revealed differences among the more protective types which could not be detected at the low ozone concentration. Tests at the low ozone concentration permitted differentiation among the less protective antioxidants not possible when testing at the high ozone concentration.

Results obtained at both ozone concentrations permitted classification of the antioxidants into the five groups shown in Table III. Those having different classifications at the two ozone concentrations are so indicated. The antioxidants in Group I provided the highest degree of ozone resistance. These were diphenyl-*p*-phenylenediamine and di-*p*-methoxydiphenylamine. The former is superior by a slight margin. Commercially prepared mixtures of these with other antioxidants are likewise excellent ozone-resisting agents. Group II lists certain ketone-amines which were found to provide good ozone resistance, and Group III shows several antioxidants which provided moderate ozone resistance. Antioxidants classified in Group IV were found to be relatively ineffective when used only to the extent of 1 part, however, as will be discussed later, certain of these—notably phenyl-1-naphthylamine, phenyl-2-naphthylamine, diphenylethylenediamine, and butyraldehyde-aniline—were found to be extremely efficient when more than 2 per cent was used. Antioxidants which produced vulcanizates having less ozone resistance than the control are shown in Group V. Within each group, relative effectiveness was difficult to establish; so the order in which antioxidants are listed in a given group is not necessarily significant.

Figure 10 shows a representative of each of these groupings after exposure for 30 minutes at the high ozone concentration and after 48 hours at the low ozone concentration.

Certain of these antioxidants were selected for testing in loaded compounds. One part of each was added to base stocks containing 40 volumes of MT carbon black, EPC carbon black, and hard clay, respectively. Tests conducted at both ozone concentrations generally showed effects similar to those noted in the

TABLE III
EFFECT OF ANTIOXIDANTS ON OZONE RESISTANCE OF
NEOPRENE VULCANIZATES

Group	Chemical name	Common or trade name
I	Diphenyl- <i>p</i> -phenylenediamine ^a	DPPD
	Dip- <i>p</i> -methoxydiphenylamine ^a	Thermoflex
II	Diphenylamine-acetone ^a	BLE, Aminox
	Phenyl-2-naphthylamine-acetone ^a	Betanox
III	Acetone-aniline ^b	Flectol H
	Acetone- <i>p</i> -aminodiphenyl ^b	Santoflex B
	Polymerized trimethyldihydroquinoline ^a	Agerite Resin D
	Symmetrical di-2-naphthyl- <i>p</i> -phenylenediamine ^{c,d}	Agerite White
	<i>p</i> -(<i>p</i> -Tolylsulfonylamido) diphenylamine ^{a,e}	Aranox
IV	Butyraldehyde-aniline ^a	Antox
	Dialkylphenol sulfide ^b	Santowhite Crystals
	Diphenylethylenediamine ^a	Stabilite
	Phenyl-1-naphthylamine ^a	Neozone A
	Phenyl-2-naphthylamine ^a	PBN, Neozone D, Agerite Powder
	Diphenylamine	
V	Heptylated diphenylamine ^b	Agerite Stalite
	2,5-Di- <i>tert</i> -butylhydroquinone ^f	
	2,2'-Methylenabis(4-methyl-6- <i>tert</i> -butylphenol)	Antioxidant 2246
	<i>p</i> -Phenylphenol ^f	Parazone
	Hydroquinone monobenzylether ^f	Agerite Alba

^a Very effective when used in greater amounts than 1%, based on the Neoprene.

^b Increases somewhat in effectiveness when used in greater amounts than 1%.

^c Becomes more effective at low ozone concentration when used in greater amounts than 1%, but not at high ozone concentration.

^d At low ozone concentration is classified in Group II.

^e At low ozone concentration is classified in Group IV.

^f Becomes more deleterious when used in greater amounts than 1%.

gum stocks. The adverse effect of fillers on ozone resistance increased the difficulty of determining the relative efficiency of the less effective antioxidants, even in the tests conducted at the low ozone concentration. This was especially the case in stocks containing clay and EPC carbon black.

EFFECT OF ANTIOXIDANT CONCENTRATION

The effect of antioxidant concentration on ozone resistance was studied. Gum Neoprene compounds containing 1, 2, 5, and 10 parts, respectively, of all the antioxidants previously studied were compared at the high ozone concentration. In most cases, as the amount of antioxidant was increased, differences in the degree of their effects on ozone resistance were accentuated markedly.

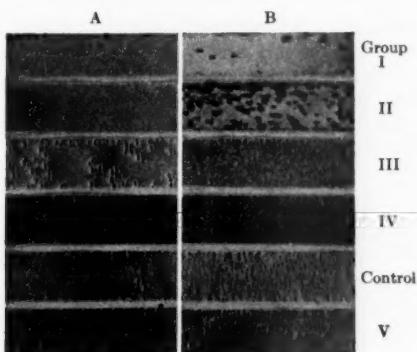


FIG. 10.—Effect of 1% antioxidant.

A. Low ozone concentration
 B. High ozone concentration

It will be noted by reference to the footnotes under Table III that certain antioxidants, which were relatively ineffective when only 1 per cent was used, became highly effective when used in larger amounts. Those which increased only moderately in effectiveness when their concentration was increased also are identified. The antioxidants listed in Group V became more injurious to ozone resistance as their concentration was increased. Two outstanding examples are shown in Figure 11. One per cent of Neozone A (chemical name listed in Table III) afforded no measurable protection after exposure for 60 minutes to the high ozone, but when 5 per cent or more was used, no cracking was induced after a 24-hour exposure. Contrarily, the compounds containing Parazone under the same test conditions became progressively worse as the antioxidant concentration was increased.

In a number of cases the comparative position of antioxidants relative to ozone resistance was reversed by changing the concentration of antioxidant and

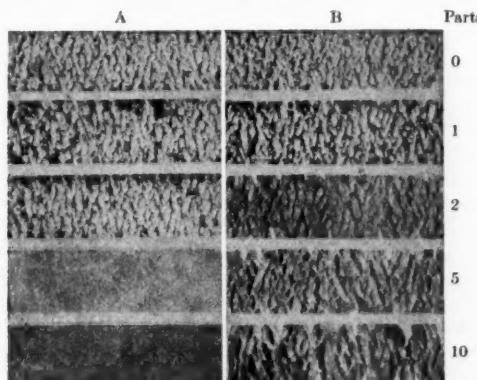


FIG. 11.—Effect of antioxidant concentration.

A. Neozone A
 B. Parazone

concentrations of ozone. An example is shown in Figure 12 in which gum Neoprene compounds containing 1 and 5 parts of Antox and Agerite White, respectively, are compared. At a concentration of 1 per cent, the stock containing Agerite White is superior to the stock containing Antox after 48-hours' exposure at the low ozone concentration. After a 1-hour exposure, at the high ozone concentration the two stocks are essentially equal. A comparison of the

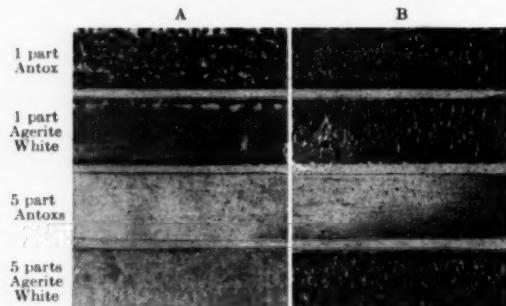


FIG. 12.—Effect of varying concentration of ozone and antioxidant.

A. Low ozone concentration
B. High ozone concentration

two antioxidants at the 5-part level when tested at the low ozone concentration shows them to be equivalent. At the high ozone concentration, however, the stock containing 5 parts of Antox is vastly superior to the one containing 5 parts of Agerite White, the latter showing no improvement in effectiveness as its concentration is increased. Because the effectiveness of some antioxidants changes, depending upon the amount of antioxidant and the ozone concentration, conclusions based on one set of test conditions will be misleading if applied to another.

TABLE IV
SOLUBILITY OF ANTIOXIDANTS IN NEOPRENE VULCANIZATES

	Per cent
Thermoflex	5
DPPD	2
Neozone D	10
Agerite White	10
Stabilite	5
BLE	10
Aranox	5
Agerite Alba	2
2,5-di- <i>tert</i> -butylhydroquinone	2
Antioxidant 2246	10
Santowhite Crystals	5
Parazone	2

Certain of the antioxidants studied were not soluble in Neoprene vulcanizates up to the maximum limit (10 parts) at which they were tested. What effect this may have had on ozone resistance is not known. The antioxidants shown in Table IV produced a visible bloom on gum vulcanizates when added to the Neoprene in the indicated amounts. The others shown in Table III apparently were soluble to the extent of 10 per cent.

EFFECT OF ANTIOXIDANTS PLUS WAXES

All of the antioxidants used in this investigation also were tested in compounds containing wax in order to determine whether the protection offered by wax would obscure the benefits derived from the antioxidants. Tests were conducted using 2, 5, and 10 parts of the antioxidants in gum Neoprene stocks containing 3 parts of Heliozone. Because of the additional protection provided by the Heliozone, it was necessary to use longer exposure periods at the high ozone concentration to induce cracking. The results show that in the presence of the wax, the differences in degree of ozone resistance conferred by the antioxidant were even more pronounced than in its absence.

In compounding Neoprene for the ultimate in ozone resistance, it is advisable to use the maximum quantity of the most protective types of antioxidants. The solubility limits generally must be recognized in order to avoid bloom. If the application permits the use of waxes, the film formed by them masks the antioxidant bloom. If it is not desired to exceed the solubility level, a blend of antioxidants is in order. A typical Neoprene cable-jacket compound having the following formula was tested:

Neoprene Type GN-A	100.0
Phenyl-2-naphthylamine	2.5 ^a
Di- <i>p</i> -methoxydiphenylamine	1.25 ^a
Diphenyl- <i>p</i> -phenylenediamine	1.25 ^a
Phenyl-1-naphthylamine	5.0
Stearic acid	0.5
Magnesia	4.0
EPC carbon black	25
Hard clay	50
Heliozone	5
Light process oil	10
Zinc oxide	10
Permalux	0.5

^a 5 parts of Thermoflex A were used.

The solubility limit of none of the antioxidants used was exceeded. This compound had exceptional ozone resistance, notwithstanding exposure at the high ozone concentration for 144 hours, after which time it was removed without having cracked.

SUMMARY

The resistance of Neoprene vulcanizates to attack by ozone as measured by accelerated tests has been studied. The known superiority of Neoprene in this property was found to be affected more by compounding ingredients than previously recognized. It was found that neither the presence of accelerators nor their influence on the modulus of fully cured Neoprene vulcanizates affected ozone resistance. The addition of fillers impaired ozone resistance in proportion to the amount used. The coarse particle size fillers were particularly harmful. Petroleum base plasticizers had a negligible adverse effect, but certain of the ester and similar types were significantly deleterious. Unsaturated vegetable oils and their derivatives, as well as wood resin, are beneficial to ozone resistance. Certain softeners and extenders frequently used to promote ozone resistance so function only by virtue of the stress relaxation they induce in vulcanizates. A number of antioxidants, especially those which reduce flex cracking are powerful ozone-resisting agents, particularly when used in large quantities. Certain of the nondiscoloring type of antioxidants are harmful to ozone resistance.

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OZONE IN LOS ANGELES AND SURROUNDING AREAS *

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For a considerable time, it has been apparent that rubber products exposed to the atmosphere in the Los Angeles area develop surface checking more rapidly than in most other parts of the United States. A plausible explanation would seem to be that ozone concentrations of the region are relatively high. Inquiry, early in 1949, failed to develop any information on surface ozone concentrations for the Los Angeles area, and it was decided to make a few orienting determinations; these were subsequently expanded to many, and the results are reported herein.

Determinations in meteorological circles by spectroscope or spectrophotometer deal with ozone in the total atmosphere, with the clear recognition that the great bulk of the measured amount is in the stratosphere or above. It is generally considered that this stratosphere ozone is by far the major source of surface ozone, which is brought down by convection currents and thereafter is subject to movement and decomposition from factors of weather, geography, photochemistry, and both natural and man-made contaminants of the lower atmosphere. It is not surprising that concentrations should vary from one location to another and from season to season.

On the basis of cracking bent rubber samples during warehouse exposure for 45 days (September 15 to November 1, 1949) Nellen, Dunlop, Glaser, and Landes¹ rated the severity of cracking at a large number of locations. Typical ratings of severity, including the extremes, were: Santa Monica, 420; Los Angeles and Denver, 360; Long Beach, Calif., 330; Dallas and Boston, 150; Washington, D. C., and Portland, Ore., 30; New York, Seattle, Atlanta, and Conshohocken, Pa., <30.

Various excellent review articles have been contributed on the action of ozone on rubber, among which may be mentioned those of Newton², of Crabtree and Kemp³, and of Fielding⁴. Crabtree and Kemp have provided the design for a convenient method of analysis.

METHOD

The apparatus employed was that of Crabtree and Kemp⁵, whose design is especially appropriate for the type of measurements desired for this study. It consists of an absorption bottle into which there is sprayed, by force of the in-

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coming air sample, a fine mist of potassium iodide, dissolved in buffer solution adjusted to pH 7. The mist partially condenses in the bottle and is then transported by the moving air sample, upward through a tube to its original reservoir, from which the solution returns to the spray orifice, to be met by fresh incoming air. The air sample is pulled by a vacuum and measured by a suitable flowmeter. The reservoir is suitably trapped to prevent loss of droplets through the vacuum outlet.

Iodine released by the ozone (or any other oxidant which may be present and effective) is then titrated with 0.001 *N* sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), using an electrometric end point depending on the depolarizing effect on platinum electrodes of minute traces of free iodine in solution.

Since potassium iodide in solution is photochemically oxidized to iodine in the presence of light, the whole apparatus was enclosed in a cardboard box



FIG. 1.—Location of test stations.

with openings only for air inflow and vacuum line. Tygon tubing was used for the inflow line. The complete apparatus was assembled without difficulty in a casing suitable for transportation and field operation.

At the fixed Los Angeles laboratory, the source of vacuum was a Hy-vac pump, and for determinations at remote points, the vacuum was obtained from the manifold vacuum line of the car.

In most cases, sampling was for a 10-minute period at the rate of 5 liters per minute. With this 50-liter sample, the titer for a 10 parts per hundred million (10^8) by volume ozone equivalent in the sample is about 0.5 cc., and using a microburet, this was handled without any particular trouble.

Replication.—Most of the data of this report are from individual, non-replicated determinations. Consecutive runs had indicated that appreciable variation of values can occur along the hourly time axis, and that replicates, if made, should be for brief measuring periods. On several occasions, checks

made in replicate for two successive 10-minute periods yielded the following pairs of results: 5.3, 5.6; 28.8, 24.4; 13.6, 15.2; and 19.3, 18.7.

Various confirmations of the general magnitude of the figures were obtained from independent determinations made by another agent. For example, on August 24, 1949, the reported figure was 44 parts per hundred million. Data taken on the same day, at 12:00 noon, by Stanford Research Institute⁶ are read from its chart as about 40.

RESULTS

A permanent sampling station was established on the roof, 30 feet above the ground, at the plant of the United States Rubber Co., located in Los Angeles,

TABLE I
OZONE EQUIVALENT AT LOS ANGELES
(By half-month periods, March 1949 to March 1950)

Period	No. of determinations	Ozone equivalent (parts/hundred million)		
		Max.	Min.	Ave.
1949				
March 1-15	4	19.6	13.2	17.4
16-31	6	19.0	9.2	11.7
April 1-15	2	26.8	20.4	23.6
16-30	5	15.2	8.4	10.7
May 1-15	5	21.7	8.0	12.3
16-31	8	30.0	10.4	15.8
June 1-15	12	41.5	8.8	25.7
16-30	10	45.8	9.0	24.6
July 1-15	—	—	—	—
16-31	12	34.5	23.0	30.5
Aug. 1-15	7	45.7	22.0	34.7
16-31	9	48.5	13.4	35.0
Sept. 1-15	8	51.0	1.6	28.8
16-30	10	46.2	20.0	31.3
Oct. 1-15	9	45.6	8.8	20.7
16-31	9	54.2	1.0	28.8
Nov. 1-15	1	—	—	16.0
16-30	6	48.5	22.2	39.2
Dec. 1-15	9	46.4	0.5	14.6
16-31	7	17.2	0.5	6.5
1950				
Jan. 1-15	5	5.8	0.8	3.0
16-31	8	39.5	0.8	19.2
Feb. 1-15	11	36.8	0.8	18.6
16-28	5	25.6	8.0	16.7
March 1-15	11	28.6	8.0	17.0
16-31	13	38.0	0.6	20.8

about 6 miles southeast of the business center of the city. The map, Figure 1, shows this location and other points of sampling to be described later.

At the permanent station, beginning early in March, determinations were made on 192 days over a period of 13 months. Some preliminary tests seemed to indicate that a daily peak period for atmospheric ozone came between 12:00 noon and 2:00 P.M., and in the main those were the periods covered.

The fluctuations from day to day were considerable. In order to picture over-all results, the data have been averaged for half-month periods, with results given in Table I. Since, as will be discussed later, it cannot be stated

that the iodine release is due exclusively to ozone, the comprehensive term *ozone equivalent* has been applied to the data obtained.

Because of interest in possible geographical and industrial factors as determinants of apparent ozone, use was made of the portability of the sample to obtain data from spots well removed from Los Angeles proper.

The United States Rubber Company operates a tire-test station about 75 miles north of Los Angeles, at Lancaster, California, on U. S. Highway 6. Lancaster is a ranch town on the edge of the Mojave Desert and is separated from Los Angeles by a mountain range of 5000 to 6000 feet elevation. One of the authors took air samples at this location with the wind blowing from the north and northwest from across the desert, with visibility unlimited, and apparently no possible chance of air contamination from the metropolitan area.

TABLE II
OZONE EQUIVALENT AT NONCITY STATIONS—1949-1950

	Ozone equiv. (parts/hundred million)	Comparable half-month, Los Angeles		
		Max.	Min.	Ave.
Lancaster, Calif.				
5-10-49	9:00 a.m.	15.2	21.7	8.0
	1:00 p.m.	19.9		12.3
8-9-49	11:05 a.m.	22.8	45.7	22.0
	12:00 Noon	25.8		34.7
	1:00 p.m.	28.9		
2-15-50	11:15 a.m.	17.4	36.8	0.8
	12:00 Noon	17.3		18.6
Morongo Valley, Calif.				
4-3-49	9:49 a.m.	10.1	26.8	20.4
	1:15 p.m.	14.2		23.6
8-10-49	1:10 p.m.	27.2	45.7	22.0
12-6-49	11:00 a.m.	17.2	46.4	0.5
1-22-50	12:30 p.m.	25.1	39.5	14.6
			0.8	19.2
Point Dume, Calif.				
5-25-49	10:55 a.m.	11.5	30.0	10.4
	12:00 Noon	20.0		15.8
	1:00 p.m.	22.6		
	2:00 p.m.	19.4		

Air samples were taken in Morongo Valley on the Colorado Desert at the base of the San Bernardino Mountains, 110 miles southeast of Los Angeles. The test spot was on the far side of the mountains from Los Angeles and the city of San Bernardino, and it is definitely not an industrial region. Other samples were taken at Point Dume on the Pacific Coast 50 miles northwest of Los Angeles.

In 1951, some measurements were made on San Antonio peak in the San Gabriel Mountains. The station was at Camp Baldy, at an altitude of 6000 feet.

The results are shown in Table II with comparable data from Los Angeles tests.

The data of Table I for Los Angeles have been assembled into a chart (Figure 2) to show the general trend of apparent ozone concentrations during 1949. Despite some irregularity, they show a considerable peak during the late

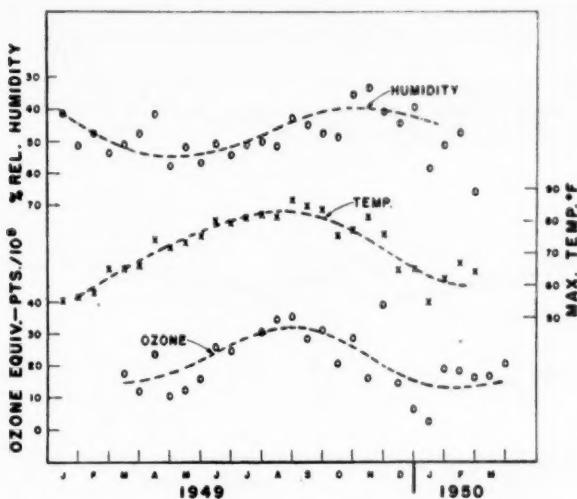


FIG. 2.—Trend lines for ozone equivalent, maximum temperature, and relative humidity at 12:00 noon in Los Angeles by half-month averages, 1949.

summer. This does not parallel the general story of meteorologists⁷ that for this latitude there is a spring peak and a fall dip in the amount of stratosphere ozone.

For comparison with the ozone equivalent trend line, daily maximum temperature data and relative humidity readings taken at noon each day at the

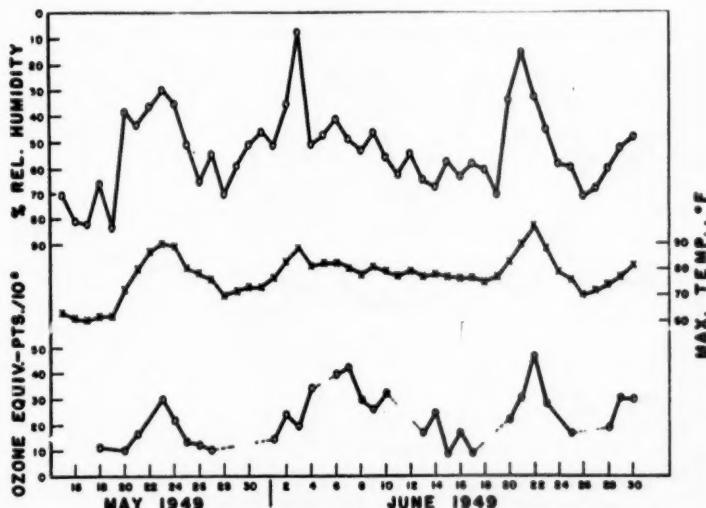


FIG. 3.—Comparison of ozone equivalent, maximum temperature, and relative humidity at 12:00 noon in Los Angeles for May and June 1949.

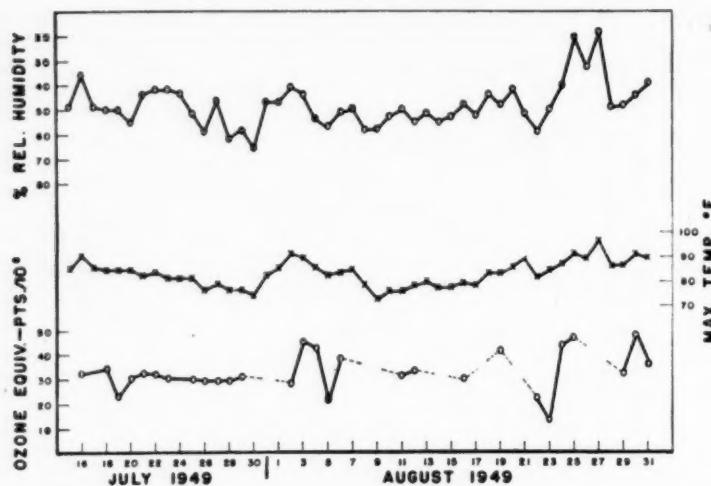


FIG. 4.—Comparison of ozone equivalent, maximum temperature, and relative humidity at 12:00 noon in Los Angeles for July and August 1949.

Los Angeles weather bureau were plotted. In these three trend curves, there is no particular correlation apparent, except for the point, possibly accidental, that the ozone peak is at the time of highest temperatures.

Although the trend lines show no correlation, this is not necessarily true of the detailed day-to-day data. Figures 3, 4, and 5 give some of the daily figures for ozone equivalent, daily maximum temperature, and relative humidity at

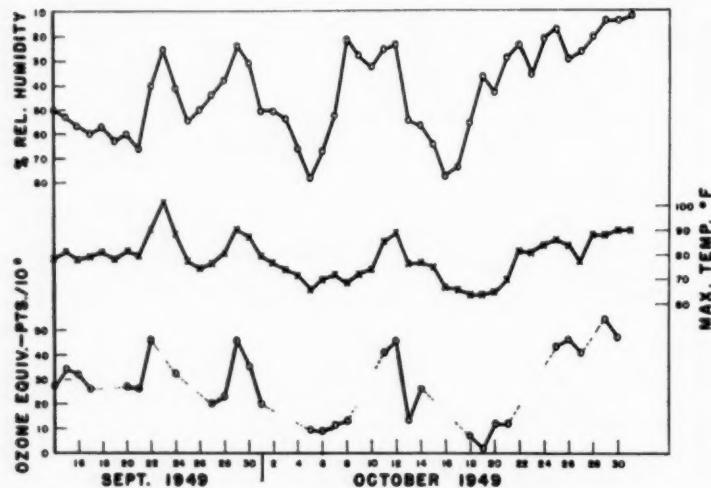


FIG. 5.—Comparison of ozone equivalent, maximum temperature, and relative humidity at 12:00 noon in Los Angeles for September and October 1949.

noon. There seems to be better than random correlation in some of the peaks of high ozone, high temperature, and low relative humidity, but no attempt has been made at a mathematical examination of this point.

Some general observations may be made regarding the data.

First, the ozone equivalent values are unusually high in most of the Los Angeles data. If the bulk of active agent is indeed ozone, it is not necessary to look further for the cause of rubber checking.

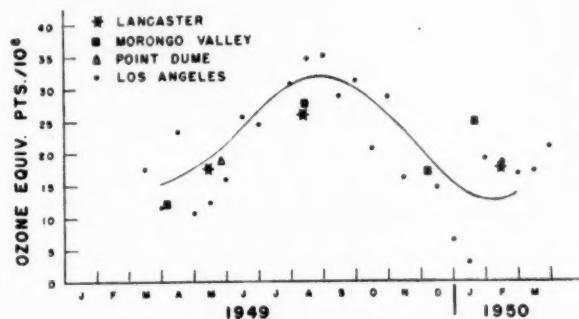


FIG. 6.—Ozone equivalent data for 1949—noncity stations vs. Los Angeles.

The high figures apply not only to Los Angeles proper, but to the several locations at some distance away, which were chosen with the thought that they would be relatively free from some of the geographic and industrial factors that might influence results in the city itself.

TABLE III
OZONE EQUIVALENT AT VARIOUS STATIONS—1951

Location	Date	No. of determinations	Ozone equiv. (parts/hundred million)		
			Max.	Min.	Ave.
Los Angeles, Calif.	May 15	1			14.9
	18-31	8	18.2	6.5	14.2
	June 2-14	2	18.5	15.1	16.8
	20-30	4	15.2	9.8	12.1
Lancaster, Calif.	July 16-30	3	17.4	14.5	16.2
	June 13	—	—	—	14.4
	29	—	—	—	9.4
Morongo Valley	June 3	—	—	—	19.0
Mt. San Antonio (6000-foot elevation)	June 8	—	—	—	19.2
Detroit, Mich.	July 3	—	—	—	17.8
	May 28	—	—	—	2.6
Washington, Mich.	June 21-28	3	2.5	1.7	2.2
	June 7	—	—	—	2.7

A picture of the relation of the data from outlying points to that of the city itself is obtained if, as in Figure 6, the average daily data from those points are superimposed on the 1949 ozone equivalent trend curve of Figure 2. (The vertical scale has been doubled in order to magnify differences.) It then becomes apparent that they fit satisfactorily in the general family of city data, except during the peak period of late summer. None of the individual values

obtained at these locations approached the values around 50 which were occasionally found at the city station. This conceivably could be due to accidental choice of the days of determinations, but one is inclined to believe that something more fundamental is involved.

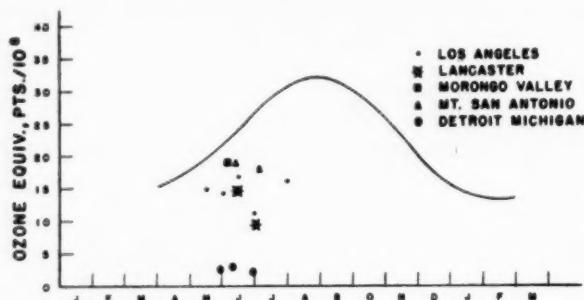


FIG. 7.—Ozone equivalent data for 1951 compared with Los Angeles trend curve for 1949.

As an item of interest, a number of new determinations were made during the summer of 1951 at some of the same locations in California and a few determinations were also made at Detroit. Detroit measurements were made on Belle Isle in the Detroit River, which in itself is a city park, but within a few miles of many industrial plants. Washington, Michigan, is a small village about 20 miles north of the edge of Detroit, in a predominantly rural district. These 1951 data are given in Table III. Their relationships to the trend line of 1949 are shown in Figure 7.

The current data have not, as yet, reached the magnitude of those for 1949. During the summer of 1951, the data from outlying points in California were in

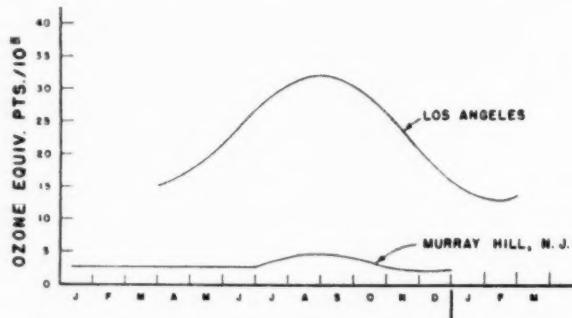


FIG. 8.—Ozone equivalent levels at Murray Hill, N. J., 1944 (Crabtree and Kemp), compared with Los Angeles, 1949.

no way discordant with those from the city station. Levels around Detroit during the same period were far below those of the Los Angeles region.

The data offered by Crabtree and Kemp³ for the year 1944 at Murray Hill, New Jersey are of interest as showing a distinctly lower level of ozone equivalent

but with something of the same peak during the late summer months. Their daily values have been estimated from their published chart, averaged by 1 half-month periods, and in Figure 8 are plotted as a trend curve in comparison with the Los Angeles trend curve for 1949.

SIGNIFICANCE OF OZONE EQUIVALENT

In the determination of ozone by iodine release from potassium iodide any oxidant, effective under the conditions used, can release iodine and thus interfere. Particularly since the ultimate amount of ozone is so small, a small quantity of any effective contaminant will give serious interference.

This warning has been stated frequently. Crabtree and Kemp⁵ discussed it, particularly with reference to oxidative interference by nitrogen dioxide, and quoted earlier authors⁶ to the effect that the interference is probably negligible in low concentrations at pH 7. Crabtree and Kemp made tests of their own, and to quote, "found by trial that nitrogen peroxide, even in concentration three- or fourfold that of the atmosphere, does not liberate iodine from potassium iodide by the procedure described". They also sought in their air samples other peroxides which would release iodine from the buffered solution, but found none. Nevertheless, they warn that possible interferences should be kept in mind.

One of the present authors performed a brief experiment which agrees with Crabtree and Kemp. Air from across the surface of beakers containing, respectively, fuming nitric acid, hydrogen peroxide, and Uniperox 60 was passed through the ozone absorber without any liberation of iodine.

In contrast to these results, Stanford Research Institute⁶ reports that nitric acid and nitrogen dioxide responded to the Kemp and Crabtree method for ozone exactly like ozone itself. They conjecture that the buffer on the spray of the droplets may have been overwhelmed by carbon dioxide or by acid impurities. Their experiment is not reported in detail.

Haagen-Smit⁹, writing within the past year in a condensed and general review of the air-pollution problem in Los Angeles, is of the opinion that ozone accounts for only a minor part of the frequently high oxidant power of Los Angeles air and discusses the complex nature of the sum total of contaminants present. He suggests mechanisms leading to the formation of nitro-organic compounds and peroxides, and he cites an experiment by C. E. Bradley of the California Institute of Technology, wherein typical ozone checking of rubber was induced by the joint effect of air, nitrogen dioxide, and sunlight.

Obviously, there is some uncertainty as to the incidence of interference, particularly as to its quantitative importance in the type of study reported here. To the authors, it seems that useful evidence may be had from consideration of the comparative data between our noncity and city stations.

Geographically, these stations are of the same region. From observation, the evidence of Nellen, Dunlop, Glaser, and Landes¹ and a great amount of quite convincing hearsay evidence, they are of the same high level with respect to the occurrence of rubber checking; in the authors' determinations they also show the same levels of ozone equivalent.

However, some of these outlying stations are outside the mountain barrier which tends to contain high concentrations of industrial contaminants in the metropolitan district, and their distance from concentrations of population and industrial activity should at least greatly reduce the magnitude of interferences discussed here.

Some separate qualitative checks were made for the presence of contaminants at these locations; although not too rigorous, the results nevertheless seem to indicate that there were no contaminants at these locations.

For nitric oxides, the Griess-Ilosvay reaction was used¹⁰. Five-liter samples of air were passed through 15 cc. of nitrogen dioxide-free water made alkaline with potassium hydroxide. The resulting solution was tested with sulfanilic acid and with α -naphthylamine to give a pink color for a positive indication of nitrogen dioxide. At Lancaster, Mt. San Antonio, and Morongo Valley, no more than traces were found, whereas a similar test in Los Angeles gave a clear test of appreciable strength.

The Stanford Research Institute¹¹ charted their determinations of nitrogen oxides for early 1949 in Los Angeles. Although peaks of 0.4 and 0.3 p.p.m. by weight were shown in the early months, from February 10 to June 10 their maxima were of the order of 0.1 p.p.m., and for the most part were much less than this. One tenth p.p.m. of nitrogen dioxide by weight is about equivalent to 6 parts per hundred million of ozone by volume, when calculated for the iodide reaction.

Analogous tests for peroxides were made at the several stations by bubbling air samples through a solution of ferrous thiocyanate in absolute alcohol¹². No color visible to the eye was ever produced at these outside stations, whereas appreciable color was produced when the atmosphere was tested in the Los Angeles area.

The inference from these tests is that if these two particular interferences were present at the outside stations, they at least were in sharply lower concentrations than in Los Angeles. If they were dominant factors in the ozone equivalent data, considerably lower figures than for Los Angeles would be expected. Reasonably, however, they may have been influential in the circumstance, noted earlier, that the maximum figures from the noncity stations did not approach the maximums for the Los Angeles station.

The fact that peroxides are present in the Los Angeles atmosphere prompted the thought that they might of themselves be agents of rubber cracking.

Accordingly, freeze-out apparatus of the design used by the Air Pollution Control District, County of Los Angeles¹³, was used to trap these materials in question. The apparatus consists briefly of five flasks connected in series. The first trap was immersed in an ice bath, the next three in dry ice and methyl Cellosolve at -80° C, the fifth and last flask in liquid nitrogen at -195° C.

On June 20, 1949, a 2-cc. sample obtained from 1800 liters of air during a 6-hour period was collected in the liquid nitrogen trap. This sample released iodine from acid potassium iodide solution in the amount which would be the equivalent of 0.6 part per hundred million of ozone on the sample of air.

Small slivers of bent rubber were exposed in a sealed container above this material in sunlight, in the dark, at 100° C, and in the neighborhood of 0° C, but no trace of cracking was ever noted. The authors are informed privately that this result with rubber parallels the experience of Haagen-Smit.

CONCLUSION

It has become rather generally accepted among rubber technologists that ozone stands alone as the cause of exposure check-cracking of rubber. Newton², Crabtree and Kemp³, and Fielding⁴ are apparently supporters of this view, and the present authors have concurred. The viewpoint, however, need not be considered as fixed. The experiment with nitrogen dioxide, cited by

Haagen-Smit⁹, raises interesting speculation of a possible exception, unless indeed the explanation lies in an intermediate formation of ozone in the system nitrogen dioxide-oxygen-sunlight. (This likelihood was suggested by Haagen-Smit in a private communication to one of the authors.)

Interesting as some of these variant possibilities might be, however, the present authors record their belief in the simple rather than the complex explanation of rubber checking in Southern California, namely, that of ozone. The general similarity of pattern between the city and noncity stations argues against any dominant effect due to special components of the city atmosphere. The general prevalence of checking in the whole area, relative to that of the country at large, is generally consistent with the high level of ozone indicated by the measurements given here. Under present information, it seems unlikely to us that effects of alternately proposed chemical agents will bulk importantly in the total effect.

The further development of information on these questions may be awaited with much interest.

ACKNOWLEDGMENT

Thanks are due various chemists who on occasion have been helpful with advice and disclosure of their own data, including A. J. Haagen-Smit and C. E. Bradley, of the California Institute of Technology; R. W. Benoliel, of the Stanford Research Institute; and P. W. Mader, of the Los Angeles County Air Pollution Control District. J. F. Hunter, D. D. Dunnom, and R. L. Francis of the United States Rubber Company, Detroit, Michigan have made useful contributions to the general subject matter of the report.

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ANALYSIS OF VULCANIZED RUBBERS. INFLUENCE OF ACCELERATORS ON THE DETERMINATION OF FREE SULFUR BY THE COPPER SPIRAL METHOD *

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INTRODUCTION

The copper spiral method is being inserted in a revised edition¹ of the "British Standard Methods of Testing Vulcanized Rubber", and this raises the question of what sulfur compounds react as "free" sulfur. In this method, "free" sulfur is considered to be that part of the sulfur which is present in the acetone extract and which reacts with a copper spiral, placed in the acetone during the extraction, with the production of copper sulfide, the amount of which can be estimated after its removal from the acetone. Since most accelerators contain sulfur, it is obvious that the presence of accelerators or accelerator fragments is a potential source of error. Fourteen accelerators of various types were therefore examined, and it was found that some react with copper, producing compounds which evolve hydrogen sulfide on treatment with hydrochloric acid.

ESTIMATION OF FREE SULFUR BY THE COPPER SPIRAL METHOD

The surface of a spiral formed from a strip of copper gauze (40-60 mesh) is cleaned by washing with concentrated hydrochloric acid, followed by washings with distilled water and acetone. The copper spiral should weigh about 5 grams, and the turns of the spiral are conveniently held in place with a loop of copper wire.

The spiral is then placed, together with the acetone, in the extraction apparatus. At the end of the extraction period, the acetone is poured off through a filter paper (to collect any loose particles of sulfide) and the spiral and filter are thoroughly washed with hot acetone.

The two are then placed in a flask in which the copper sulfide is decomposed by gently boiling for 1 hour with 100 cc. of dilute hydrochloric acid. The hydrogen sulfide is carried by a stream of carbon dioxide into a flask containing 100-150 cc. of a solution of cadmium acetate. A measured volume of standard iodine solution is then added to this solution, when the cadmium sulfide precipitate is dissolved. The excess iodine is then determined by titration with standard sodium thiosulfate.

REACTIONS OF ACCELERATORS

The accelerators used in the qualitative experiments listed in the accompanying table were purified by several recrystallizations, and the tests were carried out by heating acetone solutions of the accelerators with copper.

The formulas of the accelerators have been reproduced to show the way in which the sulfur is linked in the various compounds.

From the results shown in the table it would appear that those accelerators which attack copper can be divided into two groups.

* Reprinted from the *Journal of Rubber Research*, Vol. 19, No. 6, pages 72-73, June 1950.

(1) Salts of thioacids, namely, dithiocarbamates (1 to 6) and xanthates (7 and 8). The copper is probably attacked with the production of copper salts.

(2) Other compounds containing the C:S group. In the case of thiocarbanilide (11), copper sulfide appears to be formed on the surface of the copper, but TMT (9) and the monosulfide (10) are decomposed with the production of a dark solution, making it impossible to observe the true state of the copper surface without washing with acetone, which possibly removes any compound formed on the surface.

Sulfur in a thiazole ring and in certain disulfides is not active under the conditions of the extraction. It seems possible that MBT (13) which contains a thiol group attacks copper, but the product does not evolve hydrogen sulfide when heated with hydrochloric acid.

EXAMINATION OF VULCANIZED SAMPLES

Mixes, each of which contained one only of the accelerators already discussed, were prepared, and extracts were obtained from undervulcanized as well as fully vulcanized samples.

These extracts were examined for the presence of unchanged accelerators. Only traces of ZPD and ZDC were found whilst no TMT could be detected.

The mix containing TMT was, however, a sulfurless mix and it was possible, therefore, to have the acetone extract react with a copper spiral without interference from any elemental sulfur added to the rubber. The latter became coated with a yellow solid, which could be stripped from the copper by shaking in water. The solid dissolved in hydrochloric acid with the evolution of hydrogen sulfide and copper was detected in the solution. This was probably the compound which ZDC forms with copper, since ZDC has been shown to be present in vulcanizates derived from TMT².

Accelerator	Appearance of copper spiral	Whether H ₂ S evolved
1. Sodium pentamethylenedithiocarbamate (SPD)	Copper whitish and white ppt. formed; liquid dark	Yes
2. Piperidine pentamethylenedithiocarbamate (PPD)	Copper dull; liquid dark	Yes
3. Zinc pentamethylenedithiocarbamate (ZPD)	Copper coated with yellow solid; liquid dark	Yes
4. Cadmium pentamethylenedithiocarbamate (CPD)	Copper mainly bright; liquid pale yellow	Yes
5. Sodium diethyldithiocarbamate (SDC)	Copper unchanged; yellow ppt. formed; liquid yellow	Yes
6. Zinc diethyldithiocarbamate (ZDC)	Yellow coating on copper, black beneath; liquid dark	Yes
7. Sodium isopropylxanthate	Copper tarnished	Yes
8. Zinc isopropylxanthate	Copper tarnished; liquid yellow	Yes
9. Tetramethylthiuram disulfide (TMT)	Copper blackened; black needle crystals soluble in excess acetone; liquid dark	Yes
10. Tetramethylthiuram monosulfide	Copper dull yellow; difficult to clean; liquid dark	Yes
11. Thiocarbanilide	Copper blackened	Yes
12. A proprietary compound containing a substituted benzothiazole (Santocure)	No change	No
13. Mercaptobenzothiazole (MBT)	Copper dull yellow	No
14. Benzthiazolyl disulfide (MBTS)	No change	No

The general conclusion drawn from these and other experiments is that the copper spiral method is entirely satisfactory when only small proportions of accelerator are present, but when higher proportions are used, some interference leading to high results may be expected, the extent of which depends on the linkages of the sulfur in the compounds which either survive or arise from the vulcanization process. This interference is likely to be less than with either the nitric acid or the bromine method, the former in particular giving nearly the total sulfur content of the acetone extract³. For a low-sulfur (1.35 parts) mix with 1.5 parts of TMT, fully vulcanized, where the free sulfur content should be very low, the following figures were obtained: nitric acid method, 0.21%; bromine method, 0.12%; and copper spiral method, 0.068%. For a sulfurless mix with 2 parts of TMT and known to be much undervulcanized, and where a considerable survival of sulfur-containing material would be expected, the corresponding figures were 0.61, 0.58, and 0.22%, respectively. There is evidence, therefore, that less reaction with substances containing sulfur occurs in the copper spiral method than in some of the other methods used for the determination of "free" sulfur.

The following points of manipulative detail were noted during the course of the work.

- (1) The copper gauze should be washed well with boiling acetone after extraction, and the insoluble material removed from the surface of the copper collected on the filter paper. The gauze should be treated carefully, being handled with forceps or the like, when transferring from the extraction vessel to the decomposition flask, as the sulfide is easily removed from its surface.
- (2) Occasionally it may be found necessary to use more acid or to boil for a longer period to decompose all the sulfide.
- (3) It is essential to use 40 to 60 mesh gauze, as finer gauzes made the washing and the decomposition procedures difficult.

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DETECTION OF ELEMENTAL SULFUR IN MINUTE QUANTITIES AS IN "BLOOMS" *

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METHOD 1

Sulfur when treated in the cold with caustic soda and pyridine gives a transient blue-green coloration, which is rapidly succeeded by an orange-brown color. The test was tried in various ways. For the identification of sulfur in the bloom on a rubber article, the reaction has been adapted for use on filter paper as a spot test, the folded paper being rubbed over the surface and the reagents applied to the paper. Full instructions for carrying out the test are given below.

Effect of compounding ingredients.—None of the typical sulfur-containing compounding ingredients such as MBT, ZDC, TMT, or lithopone gave a positive color reaction with caustic soda and pyridine, nor did the presence of large amounts of the accelerators in carbon disulfide solution with sulfur materially affect the reaction, although the color took longer to appear and was generally somewhat fainter; this may, however, be merely a dilution effect. Sodium thiosulfate and sodium polysulfide likewise gave negative results; if, however, the thiosulfate is first acidified to precipitate sulfur, and then sufficient caustic soda and pyridine added, a positive reaction for the precipitated sulfur is obtained. The effect of the paraffin wax often present in bloom was determined by melting some wax, adding sufficient petroleum ether to delay crystallization, and mixing this with a solution of sulfur in carbon disulfide; the mixture was poured on to a plate, and on evaporation of solvent an artificial wax-sulfur bloom remained. A filter paper rubbed over this and treated with the reagents gave a positive reaction for sulfur.

Limits of sensitivity.—The sensitivity of the test was determined by delivery of different volumes of a 0.07 per cent solution of sulfur in carbon disulfide on to pieces of filter paper from a micropipette of total volume 0.01 cc. Provided the area of spreading of the solution was kept to a minimum (about 3 sq. mm.) a faint brown coloration was still obtained when only one microgram (1×10^{-6} g.) of sulfur was present. Such a high degree of sensitivity is not obtained by the ordinary methods of test-tube reaction, the paper tests being invariably more satisfactory than those done in test-tubes or on porcelain, as the color is more readily detectable.

Method of application.—To detect sulfur in a bloom on an article, fold in four a piece of filter paper (preferably the slow-absorbing, alkali-resistant type) and rub one of the folded edges over the surface; if the bloom is light, first treat the surface with a drop of carbon disulfide, and then rub the paper around the outline left when the solvent evaporates. Unfold the paper and add one drop (about 0.05 cc.) of strong (20 to 30 per cent) caustic soda solution, followed by one drop of pyridine. A blue-green color in the pyridine, rapidly succeeded

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by an orange or brown stain on the paper at the fold, indicates the presence of sulfur.

METHOD 2

SCHÖNBERG'S REAGENT (BENZYLIMIDO-DI-(*p*-METHOXYPHENYL)-METHANE)

This second test is carried out as follows. The substance to be tested is thoroughly ground with the reagent and transferred to a test-tube, which is then placed in an oil bath previously heated to a temperature of 210° C. After five minutes the test-tube is removed and a few drops of benzene added to the mixture. If elemental sulfur was originally present the liquid will be colored blue. On the addition of a crystal of mercuric chloride, the blue color slowly fades, while the crystal assumes a red or orange tint.

Effect of Compounding Ingredients.—The test was carried out on the substances given in the table below, with the stated results. In each case 0.01 gram of the reagent was mixed with the same quantity of the substance to be tested.

Substances tested	Colors developed by	
	Benzene solution	Mercuric chloride crystal
Sulfur	Blue	Red
MBT } all	Yellow	Colorless
MBTS } recrystallized	Greenish blue	Orange
TMT	Blue	Orange
ZDC	Pale yellow	Pale yellow
Zinc sulfide	Pale yellow	Pale yellow

Limits of sensitivity.—For this, a solution of sulfur in chloroform (0.1 mg. per cc.) was used. Portions of 1.0, 5.0, and 10.0 cc. were evaporated to dryness in a water bath and then tested as previously. From the tests it was obvious that more than 1 mg. of sulfur is required to give the proper colorations and that with diminution of the quantities of sulfur the color of the mercuric chloride crystals tends to orange, a fact which might lead to confusion of sulfur with TMT.

CONCLUSION

It appears from the tests performed that the first method given is the more sensitive and is less liable to interference from accelerators.

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DETERMINATION OF RUBBER HYDROCARBON BY A MODIFIED BROMINATION METHOD *

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An accurate method for determining the rubber hydrocarbon content of crude natural rubber is required in connection with the development of new or improved processes involved in the recovery of rubber from guayule. The bromination method, as described by Willits, Swain, and Ogg¹, has proved to be very useful in this laboratory. However, significant improvements in its accuracy have been achieved through further study of some of the factors that influence the bromination reaction. This paper reports the results of the study and recommends a modified analytical bromination procedure applicable to guayule and other natural rubbers.

In the bromination method, a solution of crude rubber in benzene is treated with a bromine solution for a given length of time. The rubber bromide formed is precipitated with ethyl alcohol, filtered into an asbestos Gooch crucible, and dried to constant weight in a vacuum oven. The weight of rubber bromide is converted to weight of rubber hydrocarbon by a known factor. If the bromine adds completely and exclusively to the rubber hydrocarbon double bonds, assuming no previous saturation, a rubber bromide of constant composition $(C_5H_8Br_2)_n$ is obtained, and the theoretical factor for conversion to rubber hydrocarbon is 0.2988. If some substitution occurs, as well as addition, the theoretical factor does not apply; and because the substitution reaction is difficult to control, it is very unlikely that a bromide of constant composition will be obtained. Willits, Swain, and Ogg¹ found a factor of 0.292 for guayule rubber, indicating that some substitution had taken place under the conditions which they employed. Edison² had previously used a factor of 0.285.

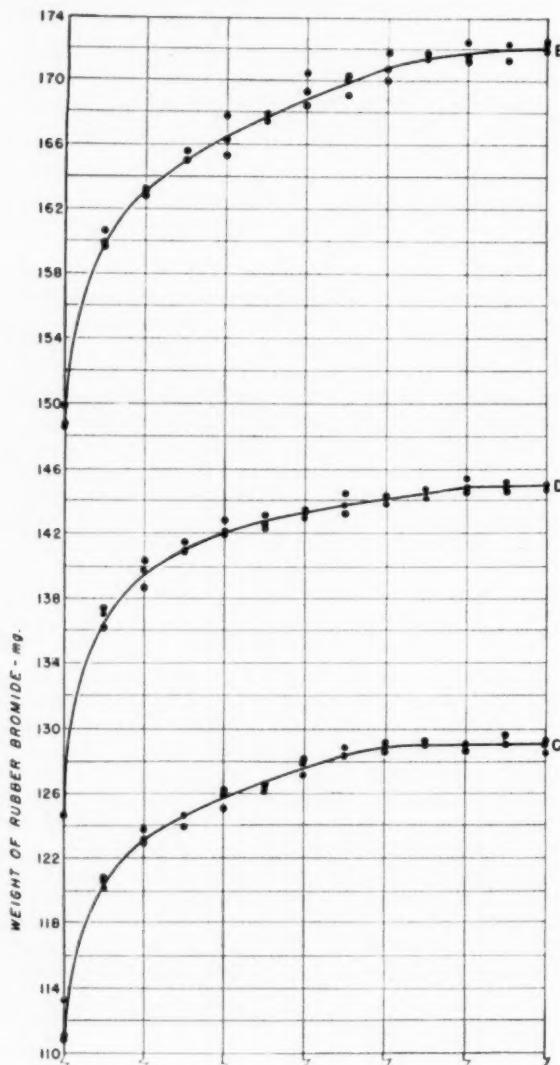
EXPERIMENTAL

Effect of chloroform on bromination.—With the bromination procedure of Willits, Swain, and Ogg¹ one of the greatest difficulties encountered in this laboratory was the inability to obtain a pure rubber bromide precipitate. Frequently some of the rubber bromide became insoluble in the brominating solution and formed a skin on the bottom of the beaker. On addition of ethyl alcohol, the precipitated rubber bromide often agglomerated into large stringy particles which occluded impurities. This precipitate usually showed a discoloration after drying at 65° C in a vacuum. Furthermore, when rubber is brominated in benzene solution, copious amounts of hydrogen bromide are evolved, which indicate substitution has taken place. The experimental factor of 0.292 confirms the evidence that a substituted product is obtained.

Bloomfield³ observed that when the bromination was carried out in the presence of chloroform, there was no agglomeration of the rubber bromide in

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the brominating solution. This was confirmed by Jones⁴ in this laboratory. Precipitation with ethyl alcohol resulted in a very fine chalk-white precipitate. Subsequent drying in a vacuum oven at 65° C produced no discoloration or change in composition. Bloomfield⁵ also stated that no hydrogen bromide is liberated when bromination is conducted at 0° C in chloroform containing 1 per cent alcohol. He interpreted this result as indicating that alcohol prevented bromine substitution. However, the authors have found that alcohol-free chloroform almost completely prevents evolution of hydrogen bromide at room



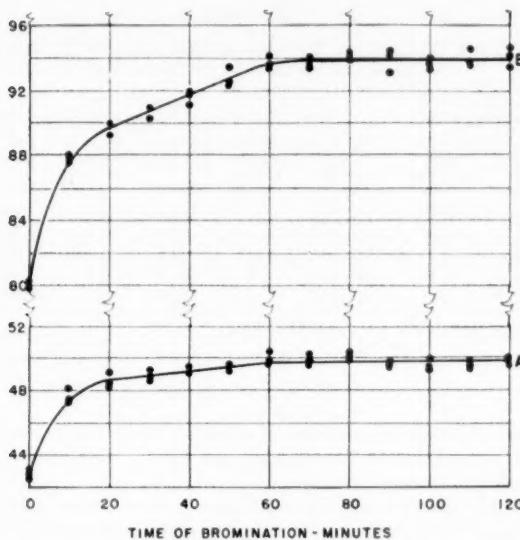


FIG. 1.—Effect of time bromination on weight of rubber bromide formed. Rubber hydrocarbon concentration mg. per 25 cc. A. 14.9 mg.; B. 28.2; C. 38.8; D. 43.6; E. 52.0.

temperature. Apparently chloroform inhibits the substitution reaction, in addition to having a solubilizing effect on the rubber bromide. This is substantiated by the fact that in the presence of chloroform we approach the theoretical factor 0.299. The amount of chloroform required in the benzene-rubber solution to prevent agglomeration usually depended on the concentration of rubber hydrocarbon being brominated, but normally an amount approximating 25 per cent of the total volume of solution was sufficient. All subsequent experiments were conducted with chloroform present in the brominating solution.

Effect of rubber hydrocarbon concentration.—Solutions of purified rubber hydrocarbon were prepared from 6-year-old guayule shrub by the following method:

The shrub was first parboiled in water at 93° C for 15 minutes.

Leaves were shaken off and discarded. The defoliated plant material was passed through a Papco ensilage cutter, followed by a Ball and Jewell fly-knife cutter. The cut shrub was dried 12 hours in a circulating oven at 65° C, and finally ground in a laboratory hammer mill to pass through a 3-mm. screen. Two-gram samples of this material were extracted with water for 4 hours followed by ethyl alcohol, acetone, and benzene for 16 hours each, using modified ASTM rubber extractors⁵. A glass thimble was used in place of the ASTM siphon cups. The benzene extract is for all practical purposes a solution of pure rubber hydrocarbon. The concentration of rubber hydrocarbon was determined by evaporating a portion of the solution to dryness on a steam bath and drying the film to constant weight at 50° C under 30 inches of vacuum. Under these conditions it is not necessary to add an antioxidant to the solution before drying to prevent gain in weight of the rubber hydrocarbon by oxidation.

TABLE I

RUBBER CONVERSION FACTORS AS DETERMINED BY RUBBER HYDROCARBON-RUBBER BROMIDE RATIO

Designation in Figure 1	Rubber hydrocarbon concn. (mg./25 cc.)		Time range covered (min.)	No. of samples brominated	Weight of rubber bromide (mg.)		Factor for converting to rubber hydrocarbon	
	Mean ^a	Standard deviation ^b			Mean	Standard deviation ^b	Mean	Standard deviation ^b
A	14.9	0.1	60-120	21	49.8	0.3	0.299	0.002
B	28.2	0.1	60-120	21	93.9	0.4	0.300	0.001
C	38.8	0.1	80-120	15	129.0	0.3	0.301	0.001
D	43.6	0.1	100-120	9	144.9	0.3	0.301	0.001
E	52.0	0.1	100-120	9	172.0	0.4	0.302	0.001

^a Mean of four or more total solids determinations.

^b Standard deviation = $\sqrt{\frac{Sx^2}{n-1}}$ where Sx^2 = sum of square of deviations from mean, and n = number of observations.

Five different benzene solutions of purified rubber hydrocarbon, with concentrations ranging from 14.9 to 52.0 mg. per 25 cc., were used to determine the effect of variations in concentration.

Rubber bromides were precipitated from each of these solutions after they had been allowed to brominate for varying periods of time ranging from 0 to 120 minutes, spaced at 10-minute intervals. The zero reading was obtained by precipitating with ethyl alcohol immediately after addition of the brominating solution, an operation which did not take over 1 or 2 seconds. Three sets of aliquots taken from each of the five rubber solutions were brominated, each set on a different day. Time of bromination was plotted against the weight of rubber bromide formed for each rubber hydrocarbon solution.

These results are shown graphically in Figure 1. All the curves reach a point beyond which further time of reaction does not appreciably change the weight of the rubber bromide formed. The bromination is essentially completed at 60 minutes for the lowest rubber hydrocarbon concentration, while 100 minutes or more are required for the highest concentration. It is apparent, therefore, that both time of bromination and concentration of rubber hydrocarbon are critical. In establishing a standard method within these ranges of rubber hydrocarbon concentration, it would be necessary to brominate the solution for at least 100 minutes to make certain a product of constant weight was obtained. Approximately 85 per cent of the bromination takes place instantaneously.

TABLE II

RUBBER CONVERSION FACTORS AS DETERMINED BY BROMINE ANALYSIS

Designation in Figure 1	Time range covered (min.)	No. of samples analyzed	Bromine (%)		Factor for converting to rubber hydrocarbon (100 - % Br)/100	
			Mean	Standard deviation ^a	Mean	Standard deviation ^a
A	60-120	4	70.2	0.1	0.298	0.002
B	60-120	11	70.4	0.2	0.296	0.002
C	80-120	5	70.0	0.4	0.300	0.004
D	100-120	4	69.8	0.1	0.302	0.001
E	110-120	4	69.8	0.1	0.302	0.001

^a See Table I.

Some of the data used in constructing Figure 1 were used in preparing Tables I and II. The fact that the conversion factor increases slightly with increased rubber-hydrocarbon concentration indicates that at the higher concentrations a very small amount of unsaturation remains although, judging from the curves in Figure 1, the addition reaction is essentially completed at the time range considered. It has become standard practice at this laboratory to select an aliquot for bromination containing 30 to 50 mg. of rubber hydrocarbon, and it is apparent that for this range the factor 0.301 can be used.

Effect of iodine in brominating solution.—The standard brominating solution contains 2 grams of iodine and 5 cc. of bromine in 100 cc. of carbon tetrachloride. In the absence of chloroform, iodine accelerates the bromination reaction, although it apparently does not inhibit substitution, in view of the hydrogen bromide given off. When chloroform is present, iodine also accelerates the bromination reaction, as may be seen in Figure 2, in which bromine-iodine solution is compared with bromine solution. The curves are within experimental error of each other after 45 minutes.

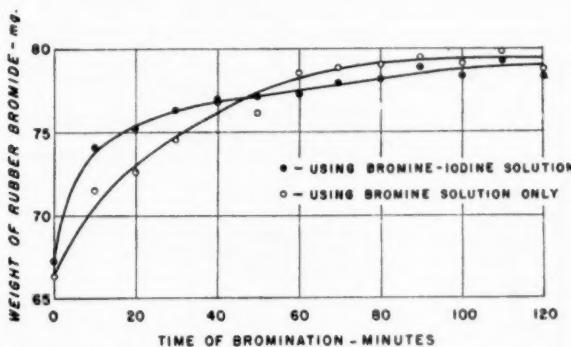


FIG. 2.—Effect of iodine on weight of rubber bromide formed.

The possibility existed that iodine was present in the rubber bromide precipitated. The Borgmann tests for iodine⁶ was applied to the products of combustion absorbed in alkaline peroxide solution as obtained in connection with the bromine determinations described below. The results were negative, although the Borgmann test is sensitive to as little as 0.2 mg. of iodide ion in the presence of 100 mg. of bromide ion.

Effect of bromine concentration.—The bromination reaction is insensitive to bromine concentration, so long as an excess is present to react with all of the rubber. In a typical bromination there is a 300 per cent excess of bromine. Doubling and tripling this amount did not increase the weight of rubber bromide formed. Willits, Swain, and Ogg¹ also found this to be true.

Effect of temperature.—The effect of temperature was not extensively investigated. Several brominations carried out at 0° C were not complete after 16 hours of reaction. Because of the high coefficient of expansion of benzene, the aliquot for analysis should be taken at the time the sample is made to volume or at a definite controlled temperature. In this work all brominations and volume measurements were carried out in a water bath at 25° C.

Effect of light.—In view of the well-known accelerating effect of light on

bromination reactions in general, all standard brominations in this laboratory have been performed under two 40-watt daylight fluorescent tubes 5 feet above the work area. Direct sunlight rays have been excluded from the solutions being brominated. A comparison is shown in Figure 3 of bromination under fluorescent lights, under fluorescent plus some sunlight through a glass window, and in the dark. It is apparent that the rubber bromide formed at the end of 100 minutes will have a different weight and compositions for each source of light. Therefore, it is essential that the light be controlled. The increase in weight due to sunlight is postulated to be the result of an acceleration of the substitution reaction, whereas the decreased weight in the dark is probably due to incomplete addition. Other sources of light were not investigated.

Effect of trichloroacetic acid.—Trichloroacetic acid is added to assist in the solution of crude rubber for analysis. It is very difficult to dissolve Hevea rubber in the absence of trichloroacetic acid without resorting to excessive breakdown. Although guayule rubber is more soluble than Hevea, trichloroacetic

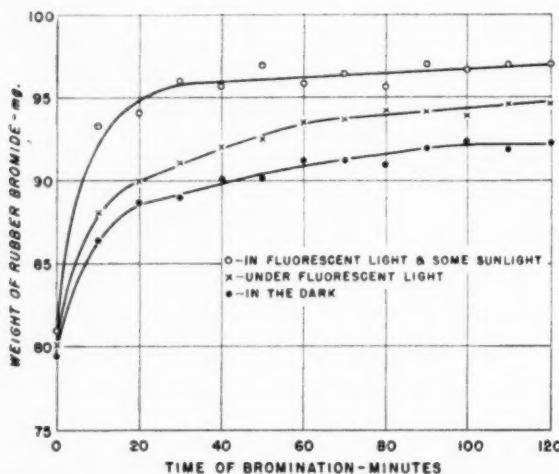


FIG. 3.—Effect of light on weight of rubber bromide formed.

acid is necessary for reducing the viscosity to the point at which the ethyl alcohol-benzene-insolubles can be centrifuged readily. As much as 1 per cent higher values for the ethyl alcohol-benzene-insolubles can be obtained by centrifuging a guayule rubber solution to which trichloroacetic acid has been added.

Fisher and Gray⁷ showed that this acid caused a slight decrease in the unsaturation of rubber. It was therefore of interest to investigate the effect of the acid on the rubber hydrocarbon determination. These results are shown in Table III. It is evident that the amount of trichloroacetic acid used in the usual procedure does not change the weight of rubber bromide over the weight of the bromide formed in the absence of the acid. Even when the acid is present in 25 times the usual amount, the weight of rubber bromide formed is reduced only very slightly.

Determination of bromine.—The bromine content of rubber bromides was determined by dry combustion in a quartz-tube apparatus. The sample, after

vaporization in a stream of air, is oxidized over quartz particles maintained at a temperature of 950° to 1000° C. The combustion products are absorbed in alkaline hydrogen peroxide and the halogen is determined by Volhard titration.

The accuracy of the bromine determination was established by analyzing the known compounds, *o*-bromobenzoic acid and *p*-bromobenzoic acid. The bromine contents obtained were 39.72 and 39.68 per cent, respectively, with a standard deviation of 0.08 for each. The theoretical value for both compounds is 39.76 per cent bromine.

Determination of conversion factor.—There are at least three methods of determining the factor for converting rubber bromide to rubber hydrocarbon. None of the methods is entirely free from error, but agreement by any two methods is considered a satisfactory check on accuracy.

The first method consists of using a purified rubber hydrocarbon solution prepared as described above, brominating a known amount of the solution, and dividing the weight of rubber hydrocarbon by the weight of the rubber bromide. Analysis of the rubber hydrocarbon film after evaporation of the benzene for carbon plus hydrogen gave a mean value of 99.49 per cent with a standard deviation of 0.03. Spence and Caldwell⁸ obtained a mean value of 99.69 per cent

TABLE III

EFFECT OF TRICHLOROACETIC ACID ON WEIGHT OF RUBBER BROMIDE FORMED

Trichloroacetic acid added (mg.)	Rubber bromide formed (mg. ^a)	
	Mean ^b	Standard deviation ^c
0	134.8	0.6
50 ^d	135.2	0.8
250	134.0	0.6
1250	134.0	0.6

^a Rubber solution used for bromination was prepared from purified Heven.

^b Mean of four replicates.

^c See Table I.

^d Amount used in standard procedure.

for similar rubber hydrocarbon films. Carbon and hydrogen determination is not conclusive evidence of the purity of the rubber hydrocarbon, however, since any impurities may be similar or dissimilar in composition.

The second method is to determine the bromine in the rubber bromide. The difference between the bromine percentage and 100, divided by 100, gives the conversion factor. In this method the assumption is made that the rubber bromide consists of only carbon, hydrogen, and bromine, which is reasonable if suitable precautions are taken to prevent contamination.

A third method, used by Willits, Swain, and Ogg¹ is to determine carbon and hydrogen in the rubber bromide. This method was not used in the present work.

Factors calculated by the first method for five different rubber hydrocarbon concentrations are shown in Table I. Factors determined by the second method are shown in Table II. Except for the values obtained with the concentration of 28.2 mg. of rubber hydrocarbon per 25 cc., the agreement between the two methods is excellent. Furthermore, the experimental factors are so close to the theoretical factor of 0.2988 that apparently no substitution has taken place.

A factor of 0.301 for guayule was selected by averaging all of the factors in Tables I and II for the range 28.2 to 52.0 mg. per 25 cc., leaving out the factor of 0.296 in Table II, which appeared to be unexplainably low.

REAGENTS

Brominating solution was prepared by dissolving 2 grams of c.p. iodine in 100 cc. of carbon tetrachloride, filtering, and adding 5 ml. of c.p. bromine to the filtrate.

Ethyl alcohol, 95%.

Benzene, A.C.S.

Chloroform, A.C.S.

Trichloroacetic acid, Eastman Kodak Co., White Label.

Benzene containing 10% trichloroacetic acid.

RECOMMENDED PROCEDURE

Preparation of sample.—Pass the crude rubber (5 to 10 grams) six or eight times through close-set cold milling rolls to blend the material and break down gel rubber, then sheet out thinly. Into a 70-cc. centrifuge tube weigh analytically approximately 0.5 gram of the blended material. Add 45 cc. of benzene and 5 cc. of 10 per cent trichloroacetic acid in benzene. Place a stirring rod in the tube and let the mixture stand 48 hours with occasional stirring to dissolve the rubber. Warm the mixture by placing the tube in a beaker of hot water. Centrifuge for 20 minutes at 2000 r.p.m.; then decant the supernatant benzene-rubber solution into a 250-cc. volumetric flask, washing the residue two or three times with benzene, centrifuging between washes, and adding the washes to the flask.

Determination of insolubles.—Wash the residue in the tube with two portions of ethyl alcohol, with thorough stirring and centrifuging. Transfer the contents of the tube to a tared asbestos Gooch crucible, wash with ethyl alcohol, and dry at 100° C for 1 hour. Weight contents as insoluble material.

Bromination.—Bring the benzene-rubber solution in the volumetric flask to volume with benzene in a water bath at 25° C. Pipet a 25-cc. aliquot at this temperature (containing 30 to 50 mg. of rubber hydrocarbon) into a 250-cc. beaker. Add 9 cc. of chloroform from a buret and 2.5 cc. of the brominating solution to the rubber solution. Place the beaker in a water bath at 25° C, and allow bromination to proceed for 100 \pm 5 minutes. No direct sunlight should come in contact with the solution in the water bath. At the end of 100 minutes add approximately 200 ml. of 95 per cent ethyl alcohol to the contents of the beaker. Allow 2 hours for the rubber bromide to settle.

Determination of rubber hydrocarbon.—Filter the rubber bromide into a tared asbestos Gooch crucible and wash the precipitate thoroughly with 95 per cent ethyl alcohol. Dry the crucible to constant weight in a vacuum oven at 65° C (requires about 1 hour). Cool in a desiccator and weigh. The weight of the rubber bromide when multiplied by the conversion factor (0.301 for guayule) is converted to rubber hydrocarbon. The percentage of rubber hydrocarbon can then be determined by dividing by the weight of the sample (MFB) and multiplying by 100.

APPLICATIONS

Rubber hydrocarbon analyses of crude guayule rubber were made to demonstrate adequately the accuracy of the rubber conversion factor 0.301, obtained with purified guayule rubber. Rubber bromides from three different types of crude guayule rubber were prepared using the modified bromination method. They were analyzed for bromine; the rubber conversion factors, calculated from

the per cent bromine found, are in good agreement with the proposed factor 0.301 (Table IV).

In the past when the constituents of crude guayule rubber were determined—rubber hydrocarbon, resins, moisture, and material insoluble in ethyl alcohol-benzene—the sum total of these components often comprised only 95 to 98 per cent of the weight of the crude rubber. As the methods of measuring the com-

TABLE IV
EXPERIMENTALLY DETERMINED CONVERSION FACTORS
FOR CRUDE GUAYULE RUBBER

Type of crude guayule rubber	No. of samples	Bromine in rub- ber bromide, (%)		Factor for con- verting to rubber hydrocarbon (100 - % Br)/100	
		Mean	Stand- ard devi- ation ^a	Mean	Standard deviation ^a
Resinous	6	70.0	0.1	0.300	0.001
Shrub deresinated	6	70.0	0.2	0.300	0.002
Worm deresinated	3	69.8	0.2	0.302	0.002

^a See Table I.

ponents other than rubber hydrocarbon are fairly reliable, the rubber hydrocarbon value was thought to be low. This was proved to be true when rubber hydrocarbon values determined by the modified method were compared with those of the former method (Table V). In all cases the total of constituents is nearer 100 per cent by the new method than by the former method.

TABLE V
DETERMINATION OF RUBBER HYDROCARBON IN CRUDE GUAYULE RUBBER

Type of crude guayule rubber	Constituents other than rubber hydro- carbon, %	Rubber Hydrocarbon, %				Total constitu- ents, %	
		Modified procedure		Procedure of Willits <i>et al.</i>		Modi- fied pro- cedure	Pro- cedure of Willits <i>et al.</i>
		Mean ^a	Stand- ard devi- ation ^b	Mean ^c	Stand- ard devi- ation ^b		
Resinous	25.2	74.2	0.2	73.5	0.3	99.4	98.7
Shrub dioresinated	7.0 3.8	92.3 94.4	0.1 0.4	90.6 92.2	0.4 0.3	99.3 98.2	97.6 96.0
Worm dioresinated	7.3 7.7	93.3 92.5	0.2 0.3	90.3 90.3	0.3 0.2	100.6 100.2	97.6 98.0

^a Mean of five replicates.

^b See Table I.

^c Mean of three replicates.

Three different types of crude Hevea rubber were brought into solution and brominated by the modified procedure. The rubber bromides obtained were analyzed for their bromine content. The rubber conversion factor determined was used to calculate the percentage rubber hydrocarbon (Table VI). It is apparent from these results that a precise determination of rubber hydrocarbon can be made on crude Hevea stock, using this method with slightly lower conversion factor. There are at least two possible explanations for the difference

TABLE VI
APPLICATION OF MODIFIED BROMINATION PROCEDURE TO CRUDE HEVEA RUBBER

Type of crude Hevea rubber	Weight of crude (mg.)	Rubber bromide (mg.)		Bromine in rubber bromide (%)		Factor for converting to rubber hydrocarbon (100 - % Br) /100	Rubber hydrocarbon			
		Mean ^a	Stand-ard devi-ation ^b	Mean ^a	Stand-ard devi-ation ^b		Mean ^a	Stand-ard devi-ation ^b	Mean ^a (mg.)	Stand-ard devi-ation ^b (%)
		51.2	163.7	0.4	70.2	0.2	0.298	0.002	48.8	0.1
No. 1										
smoked sheet										
Honduras										
smoked sheet	50.7	162.3	0.5	70.1	0.2	0.299	0.002	48.5	0.1	95.6
Pale crepe	50.2	160.9	0.2	70.2	0.2	0.298	0.002	48.0	0.1	95.7
										0.3

^a Mean of three replicates.

^b See Table I.

in the conversion factor. Guayule may be more saturated than Hevea, or contaminants in crude guayule could slow down the bromination reaction. Neither of these possibilities was investigated further.

CONCLUSIONS

Accurate and precise results can be obtained in the determination of rubber hydrocarbon by bromination if adherence to the recommended procedure is observed. The bromination reaction is sensitive to rubber hydrocarbon concentration, time of bromination, temperature, and light conditions. Addition of chloroform to the brominating solution inhibits substitution and brings the empirical factor for conversion of rubber bromide to rubber hydrocarbon close to the theoretical factor for a completely additive product.

SUMMARY

Published investigations show that, in the bromination of rubber, addition is accompanied by some substitution. The substitution portion of the bromination reaction is difficult to control and has contributed to low results and occasional poor precision. This work was carried out to investigate the effect of several factors on the bromination reaction and to find a means of inhibiting the substitution reaction. The effect of rubber hydrocarbon concentration on bromination is critical. Iodine accelerates bromination, but is not present in the final product. Temperature and light are important variables. The bromination reaction is insensitive to bromine concentration as long as a considerable excess is present. Trichloroacetic acid in the amounts used to assist in the solution of crude rubber has no effect on the results. Addition of chloroform to the benzene solution of rubber inhibits the substitution reaction with no apparent effect on the addition reaction. A factor of 0.299 for converting rubber bromide to rubber hydrocarbon is obtained for Hevea smoked sheet, which agrees well with the theoretical value. A conversion factor of 0.301 is obtained for guayule rubber, which may or may not indicate that guayule rubber hydrocarbon is slightly more saturated than Hevea. The method should have application for the direct and accurate determination of rubber hydrocarbon in crude rubber.

ACKNOWLEDGMENT

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GR-S LATEXES IN FOAM RUBBER *

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The advent of low-temperature polymerized GR-S latex has greatly benefited the foam rubber technology. Prior to the development of high-solids cold latex, foam rubber has been made, of necessity, predominantly from Hevea latex. Such GR-S latex as had been used was blended in largely for economic reasons, performing a function not much different from a diluent or extender. The superiority of cold GR-S latex over hot in all physical properties, its better wet gel strength, and the much reduced odor level¹, have made possible the manufacture of serviceable foam rubber entirely of GR-S. It is, therefore, unfortunate that, as yet, the production of cold high-solids GR-S latex is so limited.

A study was undertaken to compare the physical properties of foam rubber made from Hevea latex with foam produced from high-solids GR-S latexes, polymerized at 41° and 120° F, respectively. In addition, a number of polymer modifications were investigated in low temperature latex.

The physical properties of the foam rubber evaluated included tensile strength and elongation at break, modulus of compression, flexibility at sub-zero temperatures, and rebound elasticity.

PREPARATION OF SAMPLES

Slab foam samples of 1 inch thickness were molded at a density of approximately 0.003 pound per cubic inch.

The compounded latex was foamed by the catalytic decomposition of hydrogen peroxide and then rapidly frozen. The frozen structure was gelled by permeation with a coagulating gas, carbon dioxide. The gel was vulcanized at 215° F, removed from the mold, washed, and finally dried at 180° F in circulating hot air.

This procedure is based on a patented process.² It was found to produce consistently foam rubber of good structure from a great variety of polymers.

The standard curing formula contained uniformly 5 parts of zinc oxide, 1.5 parts of antioxidant (Agerite White), and 1.25 parts each of zinc diethyldithiocarbamate and zinc mercaptobenzothiazole per 100 parts of elastomer. The sulfur was varied from 1 to 3 parts, as indicated on the individual graphs.

Minor adjustments in soap stabilization, alkali content, and viscosity were made to compensate for variations in the colloid chemical properties of the latexes.

COMPARISON OF HEVEA, 41°F GR-S, AND 120°F GR-S

Type V GR-S was chosen as a typical 120° F latex. It was compared to a 41° F latex of the same charge ratio (70-30 butadiene-styrene) and Mooney

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viscosity (MS-4') of 53. The latter was a pilot-plant latex, made by the Copolymer Corporation as PF500-489. It is referred to as polymer 19 in Table I. Foam latex, made from 62 per cent centrifuged Hevea latex, was used as a standard of reference.

Stress-strain measurements were made by the method described by Conant and Wohler¹. The plotted results are averages of the best six out of ten data at optimum cure.

TABLE I
HIGH SOLIDS GR-S PEROXAMINE LATEXES INVESTIGATED

Ref.	Origin	Exptl. polymer number	Charge ratio (B/S)	Bound styrene (%)	Poly- meriza- tion temp. (° F)	Con- ver- sion (%)	MS-4' Mooney	Solids (%)
1	Copolymer	500-494	100/0	0	41	61	47	59.5
2	Copolymer	102-515	95/5	2.8	41	62	78	63.9
3	Copolymer	500-493	90/10	7.0	41	55	71	63.5
4	Copolymer	101-503	88/12	8.7	41	60	67	62.5
5	Naugatuck	J4437-A	87/13	11.5	50	50	15	53.0
6	Naugatuck	J4437-B	87/13	11.5	50	60	21	55.6
7	Naugatuck	J4437-C	87/13	11.8	50	70	37	49.5
8	Naugatuck	J4437-2	87/13	11.8	50	80	52	50.5
9	Naugatuck	J4668-A	87/13		50	60	83	61.4
10	Copolymer	106-539	85/15	12.0	41	50	19	63.5
11	Copolymer	106-540	85/15	12.6	41	53	30	60.5
12	Copolymer	106-538	85/15	11.9	41	50	47	62.0
13	Copolymer	102-514	85/15	11.3	41	55	62	59.9
14	Copolymer	103-534	85/15	11.8	41	49	83	62.2
15	Copolymer	108-574	85/15	12.2	41		93	62.1
16	Copolymer	101-502	80/20	15.8	41	55	38	61.4
17	Copolymer	101-510	80/20	14.6	41	58	45	63.2
18	Naugatuck	J4248	70/30		50	80	51	48.8
19	Copolymer	500-489	70/30	25.9	41	59	53	60.0
20	Naugatuck	J4168-A	70/30		50	80	64	63.5
21	Naugatuck	J4473-A	70/30		50	80	71	63.5
22	Naugatuck	J4862-A	70/30		50	80	82	60.5
23	Naugatuck	J4845-A	70/30		50	70	83	61.5
24	Naugatuck	J4828	70/30		50	60	83	60.9
25	Naugatuck	J4807	70/30		50	60	85	61.0
26	Naugatuck	J4798	70/30		50	60	86	63.5
27	Naugatuck	J4473-B	70/30		50	80	89	62.2
28	Naugatuck	J4791	70/30		50	60	91	62.4

The tensile values obtained, in pounds per square inch, were divided by the density in pounds per cubic inch, and are so plotted in Figure 1. This method compensates for minor density differences between samples, and is permissible, since the tensile-density relationship is linear within the range encountered (0.003 pound per cubic inch \pm 10 per cent).

In the left half of the graph, the foam tensile density is plotted against parts of sulfur per 100 parts of elastomer. There is a difference in the trend. The tensile strength of Hevea foam decreases with rising sulfur content, whereas both GR-S foams improve slightly.

The marked superiority of 41° F latex over 120° F latex is evident. At 2 parts sulfur the hot latex has barely 20 per cent of the Hevea-foam tensile

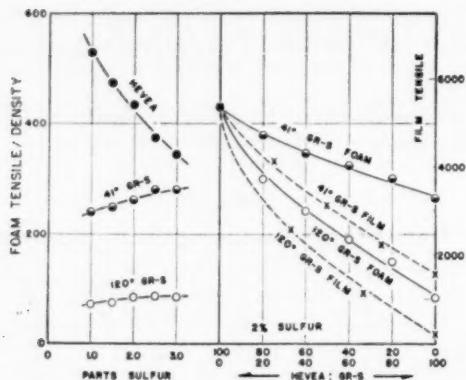


FIG. 1.—Comparison of foam and film tensile strength of Hevea with 41° and 120° F GR-S. At varying sulfur ratios and in blends.

strength. The cold GR-S foam has close to 60 per cent of the strength of Hevea foam.

In blends with Hevea (on the right of Figure 1) cold latex again proves far superior to hot GR-S. In fact, substituting one third of the natural rubber with Type V GR-S results in a tensile strength no better than that of foam made entirely of cold GR-S.

Film tensile strengths, as distinct from foam tensile strengths, were also measured on the same elastomer blends. These are shown in broken lines. In view of the known difficulty of obtaining good cast films of GR-S latex, the rolled-ring technique described by Pirot⁴ was used. A very thin film is dipped on a glass tube, permitted to dry, and then rolled into a ring. Because of the thinness of the film deposited, it dries without cracking.

While this method appears to give more consistent results in GR-S than the making of cast films, it is unfortunately not universally useful in view of the fact that some polymers adhere tenaciously to the glass, while others are too dry to roll up successfully.

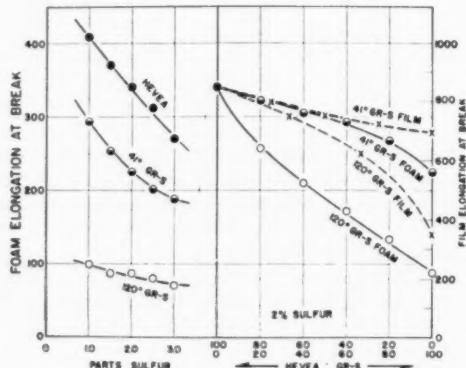


FIG. 2.—Comparison of foam and film elongation at break of Hevea with 41° and 120° F GR-S. At varying sulfur ratios and in blends.

The film tensile strength scale on the right ordinate of Figure 1, and the foam tensile strength scale on the left, were made to coincide for the all-Hevea latex compound.

No ready explanation is available for the fact that for both 41° and 120° F latex the film tensile strengths fall off more rapidly than do the corresponding foam tensile strengths, as the GR-S content is increased. It might be argued that, because of the stereo-reticulate structure of foam, the tensile property measured in a cellular material may not be true tensile strength.

Elongation at break (Figure 2) again demonstrates the marked superiority of cold over hot GR-S latex in foam. No correction for density variation between samples need be made in this instance, since the foam elongation is independent of density in the operating range. An expected trend of lower elongations with increasing sulfur ratio is observed.

On the right of Figure 2, in blends with natural rubber, replacing one third of the Hevea with hot GR-S reduces the elongation of the resultant foam to the value of foam made entirely of cold GR-S. This elongation is about two-thirds of that of Hevea foam.

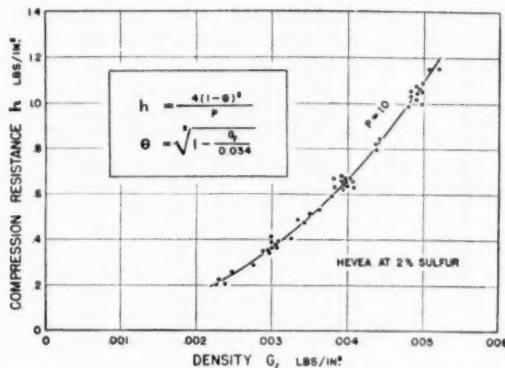


FIG. 3.—Effect of density on compression resistance of Hevea foam.

Film (rolled-ring) elongations of the same elastomer blends are shown in broken lines. Here, as distinct from tensile, the film elongations fall off less severely than do the corresponding foam elongations, as the GR-S content is increased.

An important property in foam rubber is resistance to compressive deformation. This is usually expressed as the pounds per square inch necessary to compress the sample 25 per cent of its height. It is normally measured in accordance with the indentation test described in ASTM procedure D552-46aT.

The increase in compression resistance with rising density (Figure 3) has been shown by Talalay⁵ to be satisfied by a parabolic function. The mathematical relationship between compression resistance and density is given in the formulas (insert of Figure 3), where h is the force in pounds per square inch required to produce the 25 per cent deflection, G_f is the density of foam in pounds per cubic inch, and p is a parameter which is primarily a function of the modulus of the latex compound and to a minor extent a function of cell structure. In lieu of the density G_f , a cube root function of density, θ , is substituted for con-

venience. The reference parabola shown (Figure 3) is for Hevea foam at 2 per cent sulfur, and has a p value of 10. For a given density of foam rubber, the compression values represented by the parabola ($p = 10$) are considered to be standard. Specific compression resistance of any foam sample is expressed as a percentage of standard compression. In this manner, the effect of density variations is eliminated.

As might be expected, the specific compression resistance of foam goes up with sulfur content (Figure 4).

At equal Mooney viscosity cold GR-S produces a firmer foam than the hot polymer. It is a coincidence that the specific compression resistance of 41° F GR-S foam is equal to that of Hevea foam at 2 per cent sulfur. This is due, as will be seen later, to the particular Mooney viscosity of the GR-S polymer.

In Hevea-GR-S blends small additions of Type V do not appreciably affect the specific compression resistance of foam.

The improved molecular architecture⁶ of low-temperature polymerized latex has a beneficial effect upon the elastic properties of the foam produced. This was measured (Figure 5) by the rebound of a falling ball at room tempera-

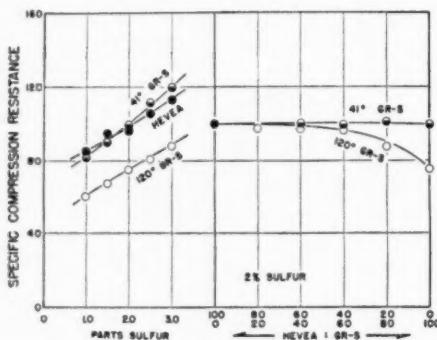


FIG. 4.—Comparison of specific compression resistance of Hevea foam with 41° and 120° F GR-S foam. At varying sulfur ratios and in blends.

ture. The rising trend with increasing sulfur ratio is shown on the left of this chart; the effect in blends with natural latex is presented on the right.

It was found that in samples of very fine cell structure, more consistent rebound data were obtained by carrying out the test in vacuum. In this manner, the pneumatic effect of air leaving and again entering the sample was eliminated. A $\frac{1}{2}$ -inch diameter steel ball was used, and was released magnetically inside an evacuated graduated glass cylinder.

The flexibility at subzero temperatures of 41° F GR-S is also superior to that of 120° F GR-S at essentially the same styrene content (Figure 6). The per cent retention of flexibility is expressed as the percentage of deflection retained when applying at the temperature of the test, the load capable of compressing the sample 25 per cent of its height at room temperature.

The test was conducted in the following manner. A specimen 4 square inches in area and approximately 1 inch thick was compressed at room temperature to 75 per cent of its original height. The load required was noted. The

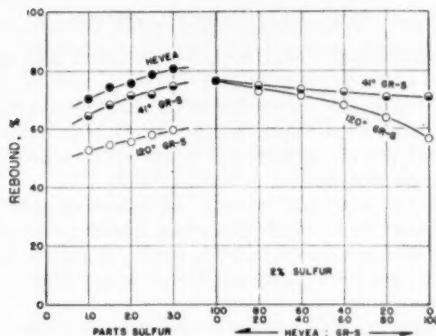


FIG. 5.—Comparison of rebound elasticity of Hevea foam with 41° and 120° F GR-S foam. At varying sulfur ratios and in blends.

sample was then conditioned for a period of 3 hours at the subzero test temperature. A new height determination was made and the same load as above applied again with the sample still in the test cabinet. Thirty seconds after load application, a new compressed height (deflection) measurement was taken.

$$\text{Per cent retention of flexibility} = \frac{\text{deflection at subzero temperature}}{\text{deflection at room temperature}} \times 100$$

At the less severe test temperature of -40° F, increased sulfur has a beneficial effect on the flexibility of Hevea and cold GR-S. This effect is lost at -70° F.

In blends with natural rubber, it is evident that the elastomer of poor flexibility has a dominant effect. For example, the substitution of a little over 10 parts of Hevea with 120° F GR-S reduced the flexibility of the blend to that of a foam made entirely of 41° F GR-S latex. This holds true at both test temperatures of -40° and -70° F.

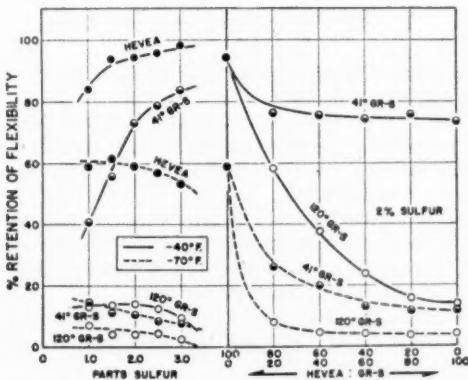


FIG. 6.—Comparison of flexibility at sub-zero temperatures of Hevea foam with 41° and 120° F GR-S foam. At varying sulfur ratios and in blends.

POLYMER MODIFICATIONS

The comparison of foam properties has been based thus far on a single low-temperature latex, which is polymer 19 in Table I, and has 26 per cent bound styrene, a small rotor Mooney viscosity of 53, and a conversion of 59 per cent.

In order to ascertain the effect of different styrene contents, Mooney viscosities, and percentages of conversion, the 28 experimental polymers shown in Table I were selected and studied in foam rubber.

They are primarily arranged in order of ascending styrene charge ratios, and within each group, in order of increasing Mooney viscosities (MS-4').

The polymers were produced in pilot plant quantities by the Naugatuck Synthetic Division, and the Copolymer Corp., respectively, and are identified with their pilot plant number.

All polymers were made in high solids peroxamine recipes⁷, at either 41° or 50° F, as indicated, and emulsified in a fatty acid soap-Daxad system.

As indicated in the last column of Table I, most latexes were received as heat concentrates at around 60 per cent total solids. A few, such as polymers 5, 6, 7, 8, and 18, were received unconcentrated at lower solids. These were creamed to approximately 60 per cent before using.

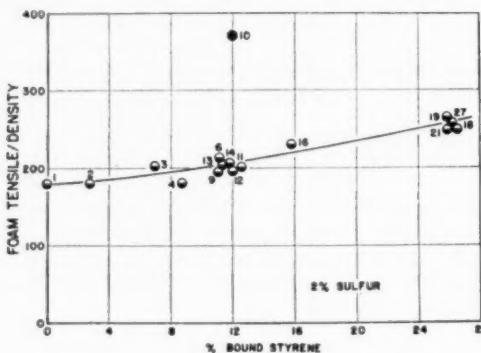


FIG. 7.—Effect of styrene content on foam tensile.

In succeeding charts, these polymers are referred to by the order number given in the first column of Table I.

It was found that, generally, one particular polymer variable dominates a specific physical property. As an example, the styrene content of a low-temperature latex dominates two properties of a foam—the tensile strength and the flexibility at subzero temperatures.

The bond styrene content of a low temperature polymer has essentially linear effect on the tensile of the foam (Figure 7). However, the effect is not as great as might be expected. Reducing the styrene content from 26 to 11 or 12 per cent lowers the tensile by only 20 per cent.

The styrene content *vs.* foam tensile strength correlation is generally satisfactory except for polymer 10 which exhibits abnormally high tensile strength at 12 per cent bound styrene.

In a preliminary attempt to shed light on this discrepancy, it was found that, despite its low Mooney viscosity, MS-4' of 19, the unmilled polymer is not free

of gel. In addition, the soluble portion appears to have an unusually narrow molecular-weight distribution, as indicated by fractional precipitation from benzene solution. Work on this phase is continuing.

Styrene content has a major bearing on the flexibility of foam at subzero temperature. It has previously been shown⁸ that reducing the styrene ratio

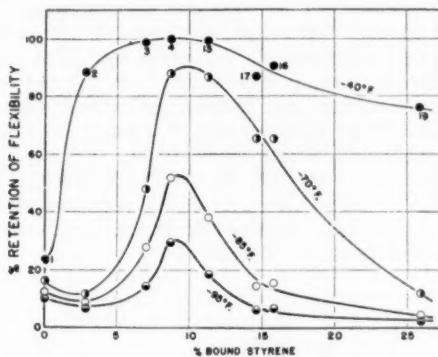


FIG. 8.—Effect of styrene content on flexibility of foam rubber at subzero temperatures.

in a polymer improves its flexibility at low temperatures. Eight styrene levels from 0 to 26 per cent, as represented by polymers 1-4, 13, 16, 17, and 19, were investigated at 2 parts of sulfur (Figure 8).

A definite optimum was found to exist at around 10 per cent bound styrene. The trend persisted down to the lowest test temperature investigated, -95° F . At this optimum styrene level, foam rubber can be made which is completely

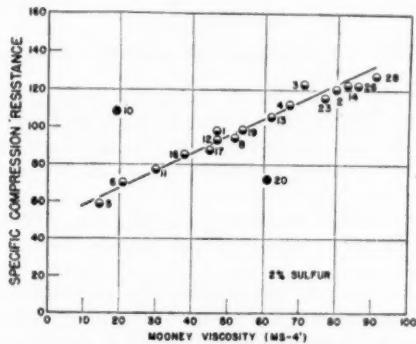


FIG. 9.—Effect of Mooney viscosity on specific compression resistance of foam rubber.

flexible at -40° F , is more flexible than Hevea foam at -70° F , and still retains an appreciable degree of flexibility at -95° F .

The flexibility was measured in the test cabinet after conditioning the sample for 3 hours. This exposure is long enough to ensure uniform temperature throughout the samples and probably also to crystallize the more readily

crystallizable polymers. It may be too short, however, for all long-term crystallization effects to take place.

A clear-cut linear relationship appears to exist between the Mooney viscosity of a low-temperature polymer and the specific compression resistance of the resultant foam (Figure 9).

Mooney viscosities from 15, small rotor, to 90, small rotor, were investigated and are plotted at 3 per cent sulfur. The specific compression resistance more than doubles in this range. The 1 and 3 per cent sulfur lines would lie parallel and equidistantly below and above the 2 per cent sulfur line shown.

The fact that the relationship is dominated by Mooney and is essentially independent of styrene content can be inferred by comparing polymers 1, 8, and 19, which at practically identical specific compression resistance contain 0, 11, and 26 per cent bound styrene, respectively.

Two of the polymers, 10 and 20, do not fit the trend. Polymer 20 was highly cross-linked with divinyl benzene during polymerization, and contains 80 per cent of very tight gel. Polymer 10 is the same polymer which gave abnormally high tensile strengths in Figure 7.

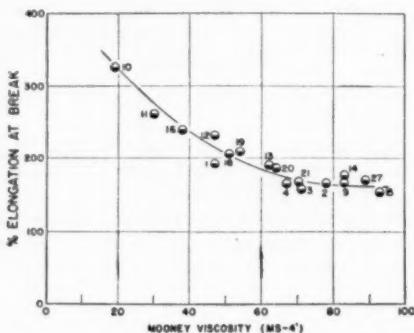


FIG. 10.—Effect of Mooney viscosity of cold GR-S on elongation at break of foam rubber.

Mooney viscosity also dominates the elongation at break of low-temperature GR-S foam. The trend is shown in Figure 10 for foam rubber vulcanized with 2 per cent sulfur. As the Mooney viscosity is increased, the elongation at break falls off. This reduction appears to level off at about 70 small-rotor Mooney.

Again, the styrene content is not a major influence. Polymers 3 and 21, of practically identical Mooney viscosity and elongation, contain 7 and 26 per cent styrene, respectively.

The effect of conversion on the stress-strain properties is a controversial issue. While it can be shown that, in high solids cold GR-S latex, film properties decline with higher conversion¹, it has not been possible to show this effect in foam rubber. Two conversion series, one at a 70-30 butadiene-styrene charge ratio and constant Mooney viscosity, the other at an 87-13 charge ratio and varying Mooney viscosities were investigated in low temperature GR-S foam (Figure 11). The 70-30 series ranged from 60 to 80 per cent conversion, the other from 50 to 80 per cent.

Both lines lie at appropriate tensile levels for their respective styrene contents, but fail to show any significant trend with conversion. The broken line,

on the other hand, which shows film tensile strengths of the 70-30 polymers, falls off significantly with increasing conversion. Here, again, is an instance of poor correlation between film and foam properties.

Considerable interest has focused recently on oil-modification of high Mooney cold GR-S in solid rubber⁹. Increasing amounts of Circosol-2xH were incorporated into a foam rubber recipe. A low temperature GR-S latex

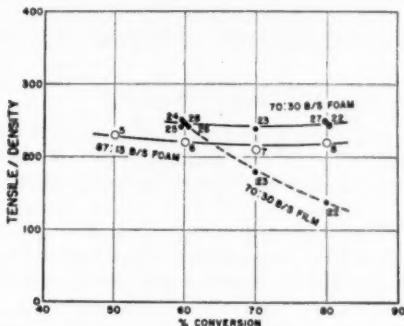


FIG. 11.—Effect of per cent conversion on tensile strength of cold GR-S foam rubber.

with a small rotor Mooney of 91 (polymer 28, Table I) was used in this series. This polymer had a gel content of 36 per cent.

The elongation at break increases substantially, from about 200 to 400 per cent by the addition of 50 parts of Circosol-2xH per 100 parts of polymer. At the same time, the specific compression resistance drops substantially. It crosses the 100 (Hevea) reference line at about 13 parts of Circosol. The foam

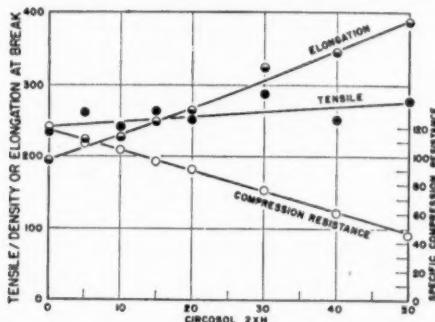


FIG. 12.—Effect of oil-extension of a high Mooney-cold GR-S latex on foam properties.

tensile strength is affected surprisingly little. In fact, it appears to increase very slightly.

SUMMARY

The superiority of cold GR-S high-solids latex over latex polymerized at 120° F has been demonstrated in foam rubber in terms of greater tensile strength, better elongation at break, higher modulus, improved rebound elas-

ticity, and enhanced low temperature properties. The magnitude of the effect observed is far greater than the corresponding improvement reported in tire tread stocks¹⁰. A number of polymer modifications in low-temperature polymerized latex were investigated. It was shown that, by the proper choice of styrene content (approximately 10 per cent bound), GR-S foam rubber superior to Hevea foam in subzero properties can be made. The modulus of foam rubber improved significantly with rising Mooney viscosity of the contained polymer, while the elongation at break was affected adversely. The degree of conversion was found to have little bearing on the properties of the resultant foam rubber.

ACKNOWLEDGMENT

The authors wish to express their appreciation to L. H. Howland and V. C. Neklutin of the Naugatuck synthetic plant, and to J. P. McKenzie of the Copolymer Corp., for making this study possible by providing the experimental latexes.

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FILM FROM MIXTURES OF NATURAL AND SYNTHETIC RUBBER LATEX

PHYSICAL PROPERTIES *

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The principal tonnage uses of GR-S-type latexes, aside from tire cord adhesives, are in products in which natural-rubber latex is the principal or an important component. The amount and type of synthetic latex used in blends of commercial importance have been influenced by economic factors and by the processing and physical properties of the product, but more often the synthetics have been looked upon chiefly as "extenders" for the natural latex.

However, with the introduction of the so-called cold rubber latexes, there has been much evidence that the use of synthetic rubber latexes may now be extended into these applications as 100 per cent synthetic, and the products will have useful physical properties somewhat comparable to those made using natural-synthetic rubber blends.

No comprehensive evaluation of the effect of the several polymerization variables on the vulcanized film properties of natural rubber-GR-S blends has been reported, although studies on some aspects of this problem have been described¹. A preliminary study of the variables of butadiene-styrene ratio, polymerization temperature, percentage conversion, and Mooney viscosity, on the properties of blends varying from 0 to 100 per cent synthetic content, has been undertaken. In this initial phase of the study attention has been confined to those variables affecting only the polymer properties, and the so-called latex properties—amount and type of surface active agents, catalysts, particle surface unsaturation, pH, etc.—have been varied, of necessity, over fairly wide limits in order to make possible the preparation of latexes of the desired range of polymer characteristics. Further, the study was confined to a more or less uniform evaluation procedure, rather than an attempt to develop casting, drying, and curing conditions which are optimum for each latex. The evaluation technique used adheres closely to procedures which have been widely practiced in the latex industry for years².

The restriction of the scope of the evaluation procedure and the comparative lack of uniformity in the colloidal and other nonpolymer properties of the latexes will, it is realized, fail to bring out the maximum potential properties of many of the polymers. Such compromises were necessary in a preliminary program of this nature in order to keep the variables within a practical number. It was felt, moreover, that the evaluation should roughly approximate the conditions of use, and that methods that were completely unattainable in commercial practice should not be employed. This eliminated from consideration

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certain techniques which had been observed to give improvements in sheet properties, such as casting the sheet in special atmospheres, drying in vacuum desiccators, curing at low temperatures, and the like.

An important property which has a considerable influence on the technical usefulness of a latex, but which is not easily controlled or susceptible of precise measurement, is its ability to form well-knit, strong sheets during drying or when treated with gelling agents, i.e., prior to cure. This property is commonly known as wet gel strength, and reflects the effects of a large number of variables of the polymer, latex colloidal properties, pretreatment, viscosity, drying environment, and so on. Natural-rubber latex is outstanding in exhibiting high wet-gel strength under an extremely wide variety of conditions of use, whereas GR-S synthetics have been very erratic in this respect. Several techniques have been developed which help to overcome this deficiency of the GR-S synthetic latexes in the manufacture of frothed sponge³. The attainment of high vulcanizate strength in cast latex sheets is usually tied in with the attainment of high wet gel strength under the conditions of use. Thus, high vulcanizate strengths on cast latex films of cold GR-S rubbers have been obtained in some cases⁴, but they have often been found difficult to reproduce from one laboratory to the next. Also, widely variable results have been obtained by the same investigators on supposedly similar latexes, as has been the experience in this laboratory. The evaluation technique used has failed to obtain any of the tensile strengths of 2000 to 3000 pounds per square inch which have occasionally been obtained by others on cold rubber latexes.

PROCEDURES

Latex Preparation.—Most of the high-temperature latexes were prepared in a base recipe and with a procedure similar to that used for preparing Type V latex⁵. One hundred parts of monomer was charged into a reactor equipped with a high displacement agitator containing 50 to 60 parts of water, 0.5 to 1.0 part of carboxylic acid soap, 0.3 part of potassium persulfate, and an amount of normal or tertiary dodecyl mercaptan adjusted to give the desired Mooney viscosity. Increment addition of soap solution after 15 per cent conversion was used to maintain latex stability, a total of 3 to 4 parts of soap generally being present in the final latex. The soaps were mixtures of sodium or potassium salts of oleic and rosin acids. Particle diameters of latexes so produced are of the order of 2000 to 3500 Å, as determined by soap titration⁶, and are classified as large particle size latexes in comparison with the much smaller sizes, 600 to 900 Å diameter, obtained in the polymerization recipes used for making latex to be processed into dry rubber.

A few high temperature latexes were prepared in a recipe giving a small initial particle size, *viz.*, a recipe similar to that used for making Type II latex, and were agglomerated with acetic acid and ammonia⁷ to particle sizes comparable to those obtained with the large particle size procedure outlined above. These latexes were creamed from 15 to 20 per cent solids to 45 to 55 per cent solids with 0.1 to 0.3 per cent ammonium alginate (on the water phase) prior to use.

Low-temperature latexes were prepared in a polyamine-hydroperoxide high solids type of recipe, which the U. S. Rubber workers pioneered and which is being currently produced⁸ as X-635.

Shortstopped latexes were vacuum-stripped to remove residual styrene prior to use.

TABLE I—PRINCIPAL POLYMERIZATION VARIABLES AND PROPERTIES OF LATEXES USED

Latex identification	Type of recipe ^a	Polymerization temperature (° F) ^b	Reactor size ^c	Monomer charge (B-S) ^d	Combined styrene (%)	Conversion (%)	Mooney viscosity (MS benzene volume of gel (%)	Solubility in swelling benzene (%)	Figures in which data used
P3375-V93	Type V	122	100-0	95	86	13	21	6.7, 8, 13, 14	
P3375-V79C	Type V	122	100-0	60	48	51	3, 4, 6, 7, 8		
P4381 ^e	Type V	122	100-0	60	108	30	34	5	
P3375-V79B	Type V	122	100-0	40	42	48	95	6, 7, 8	
P3375-V76A	Type V	122	100-0	25	52	29	76	6, 7, 8	
Type VII ^f	Commercial	122	80-20	90-95	24	41	26	11, 12, 13, 14	
P1986-34	Type V	122	80-20	18.5	95	72	24	22	11, 12
Type V ^g	Type V	122	70-30	29.5	95	65	10	19	1, 2, 8, 13, 14
Type V ^g	Type V	122	70-30	27.4	60	61	38	62	1, 2, 5, 8, 9, 10
Type V ^g , low conversion	Type V	122	70-30	60	100	26	24	9, 10	
P3490-18 ^g	Type II	122	70-30	53	52	63	123	9, 10	
RXL-3902	Type V	122	70-30	50	14	72	75	9, 10	
RXL-3908	Type V	122	70-30	34	74	28	67	8	
RXL-3938	Type V	122	50-50	49.0	60	35	63	5, 8	
Chemigum 101A ^g	Type V	122	45-55	54.0	95	60	26	18	8, 13, 14
P4487-8	Polyamine hydroperoxide	50	100-0	60	40	100	3, 4		
RXL-3928	Type V	Small	50	70-30	32.0	87	75	42	1, 2
J4387D ^h	Polyamine hydroperoxide	50	87-13	80	44	64	82	15, 16	
J4248B ^h	Polyamine hydroperoxide	50	70-30	80	65	53	58	15, 16	
X-547 ^h	Iron-hydroperoxide	Commercial	50	70-30	26.4	60	50	82	1, 2, 5, 15, 16
J4248D ^h	Polyamine hydroperoxide	50	70-30	60	57	69	120	15, 16	
J3630D ^h	Iron-hydroperoxide	50	70-30	60	39	84	84	15, 16	
P4427-1	Polyamine hydroperoxide	Large	50	70-30	60	78	65	80	15, 16
RXL-3935	Polyamine hydroperoxide	Small	50	50-50	46.7	65	74	56	119

^a Recipe: 1. Type V described in text.2. Type II, standard hot GR-8, 100 monomer, 180 water, 5.0 soap, 0.3 K-SiO₃, n-dodecyl mercaptoan modifier.3. Iron hydroperoxide, X-547 type, 100 monomer, 65 water, 3.0 potassium soap, 1.5 potassium salt of sulfonated naphthalene-formaldehyde condensation product, /n/-dodecyl mercaptoan modifier; amounts of alkyl hydroperoxide, iron sulfate, K₂P₂O₇, and Na₂SO₄ adjusted to give desired reaction rates.

4. Polyamine hydroperoxide X-635 type, 100 monomer, 70 to 80 water, 3.0 potassium soap, 1.5 alkali salt of sulfonated naphthalene-formaldehyde condensation product, /n/-dodecyl mercaptoan modifier; amounts of alkyl hydroperoxide and alkylene polyamine adjusted to give desired reaction rates.

^b Small, 5 or 20 gallons, 1 barrel, 1600 or 2500 gallons.^c Many of the latexes listed were being polymerized at 122° F, and carried to 135° or 140° F when necessary to reach high conversions.^d Produced in RRC plants as X-3911.^e Andover, Mass. ^f Production latex. ^g Goodyear Tire and Rubber Co., Chemical Division.^h Office of Rubber Reserve, U. S. Rubber, Naugatuck, acting as agent of Rubber Reserve.

The natural rubber latex was an ammonia-preserved *Hevea* latex from the Goodyear plantation in Sumatra, concentrated by centrifuging. It was similar in properties to the regular concentrated natural rubber latexes of commercial use.

Tests on latex and raw polymer.—Latexes were examined for mechanical stability, pH, and approximate particle size before acceptance for use. The particle size estimate was based on a turbidity measurement⁵, and served simply to eliminate latexes of too small a particle size. A few particle sizes by soap titration were run to confirm the particle sizes obtained by turbidity measurements. Mooney viscosities (small rotor, 1½ minutes) were determined on very lightly milled salt-acid coagulated samples to which antioxidant had been added. Solubility in benzene and swelling volume of the gel were measured by leaching unmilled crumbs in benzene, 1 gram per 100 cc., at room temperature for 20 to 40 hours without agitation, and filtering the soluble portion through 80-mesh screen. The solubility was determined from a dried down aliquot of the filtrate, and the swelling volume of the gel was estimated from the volume of swollen material—the difference between the initial and filtrate volumes—and the known weight of gel. These parameters provide useful information con-

TABLE II
COMPOUNDING RECIPE FOR EVAPORATED SHEET SAMPLES

Material	Parts by weight
Rubber, latex solids	100
Potassium oleate	0 to 1.2
Potassium hydroxide	0.5
Agerite White	1
Sulfur	1
Zinc oxide (XX-50)	1
Zinc diethyldithiocarbamate	1
Ammonium alginate	0 to 0.1

cerning macrostructure which is not furnished by the Mooney viscosity or other rheological tests.

The latexes used and their principal properties are enumerated in Table I.

Preparation of cast latex sheets.—For convenience and simplicity, the evaporated sheet method was used for comparing the physical properties of the latex rubbers. This method consisted of stabilizing the latexes with a soap and potassium hydroxide so that when mixed together, they remained fluid. The compounding ingredients consisting of sulfur, zinc oxide, accelerator, and antioxidant, were added as a mixture of dispersions in water and thoroughly stirred into the blended latexes (Table II).

The latex mix of 50 to 58 per cent total solids was matured 16 hours at room temperature without agitation. The viscosity of the mix was then increased by the addition of a thickening agent such as ammonium alginate, and a sufficient quantity was poured onto a glass plate framed by glass strips to make dried sheets of 9.25 × 6.50 × 0.060 inches. The drying of the latex was controlled at a temperature of 75° to 80° F for 16 hours in a confined space to maintain high humidity, after which the almost dry sheets were stripped from the glass and allowed to dry for 7 days at the same temperature.

The dried rubber sheets were cured in an air oven at 212° F for 5, 10, 15, 20, 30, and 40 minutes.

The sheets were then conditioned for at least 24 hours in a room at 50 per

cent relative humidity and 77° F before determining their physical characteristics.

Preparation of milled sheets.—The milled rubber test sheets were made by mixing the antioxidant dispersion into either the latex or latex blend and then pouring the latex on glass plates, 36 × 36 inches, framed by glass strips. The latex was dried at 75° to 85° F for approximately 24 hours, after which the rubber sheets were stripped from the glass and hung up for additional drying at the same temperature for 3 days. The sheets were approximately 0.04 inch thick.

These sheets were further compounded on the conventional two-roll rubber mill by the addition of sulfur, accelerators, zinc oxide, and stearic acid (Table III). The fully compounded slabs of rubber were then allowed to set for 24 hours, after which they were cut into test-pieces to fit the mold cavity of $4\frac{1}{2} \times 6\frac{1}{2} \times \frac{3}{2}$ inches. The vulcanization was done in the conventional laboratory press at 275° F for 10, 20, and 30 minutes, after which the sheets were allowed to condition at 77° F for 24 hours before they were cut into the same size dumbbell strips as used for the evaporated latex sheets. The test strips were condi-

TABLE III
COMPOUNDING RECIPE FOR MILLED RUBBER SAMPLES

Material	Parts by weight
Rubber, latex solids	100
Stearic acid	1
Agerite White	1
Zinc oxide	1
Sulfur	1.6
Captax	0.675
Diphenylguanidine	0.825

tioned 24 hours at 50 per cent relative humidity and 77° F before stress-strain determinations were obtained.

TESTING

The stress-strain data were obtained using a dumbbell-type test strip having a center section of 2.50 × 0.394 inches. This differs slightly from that specified by ASTM, as it was designed especially for the Albertoni autographic machine. The horizontal-type autographic machine, with a speed of jaw separation of 30 inches per minute, was used, and the stress-strain curve was plotted automatically. The advantage of this type of machine was that modulus determinations could be easily obtained at all elongations.

The tensile and elongation data used in the figures were picked from the best cure of the range mentioned above. Thus, in Table IV, the 15-minute cure for the natural rubber, the 5-minute cures for the Type V and X-547 latexes, and the 5- and 15-minute cures for the 50-50 natural rubber-synthetic blends of Type V and X-547, respectively, would be chosen.

The Gehman torsional flexibility apparatus was used in obtaining the low temperature properties of the rubbers⁹.

RESULTS

Before discussing the data it is appropriate to point out the difficulty of predicting the modifier requirement accurately enough to obtain a desired Mooney viscosity within closely set limits when other variables are also being

TABLE IV
STRESS-STRAIN DATA FOR SEVERAL POLYMERS AND BLENDS OVER RANGE OF CURES

Natural rubber	70-30 Butadiene-styrene hot (Type V)				70-30 Butadiene-styrene cold (Type X-547)				50-50 Natural-type V				50-50 Natural-type X-547				
	Tensile strength (lb./sq. in.)		Ultimate elongation (%)		Tensile strength (lb./sq. in.)		Ultimate elongation (%)		Tensile strength (lb./sq. in.)		Ultimate elongation (%)		Tensile strength (lb./sq. in.)		Ultimate elongation (%)		
Vulcanization (minutes at 212°F)	At 600%	At	break	At	break	At	break	At	break	At	break	At	break	At	break	At	break
0	980	3350	375	310	200	290	250	900	1050	200	690	1225	650	900	840	1225	250
5	930	3800	500	620	260	225	720	426	250	625	1100	900	975	735	1475	250	
10	875	3825	620	4150	600	675	290	700	475	300	620	1100	900	975	1975	400	
15	920	20	930	4125	20	850	3850	650	900	230	620	1050	630	1050	925	1725	335
25	900	3825	600	220	200	200	200	600	230	200	630	975	610	950	900	775	900
40	865	3825	575	600	200	200	200	600	230	200	630	975	610	950	900	775	900

manipulated. Consequently, all polymers having Mooney viscosities within certain ranges were considered to be equivalent, these ranges being roughly divided as follows: high, 70 MS and higher; medium, 40 to 70 MS; and low, below 40 MS. The authors have been reluctant to adopt the Mooney viscosity as the sole measure of molecular size and toughness, since it fails to distinguish

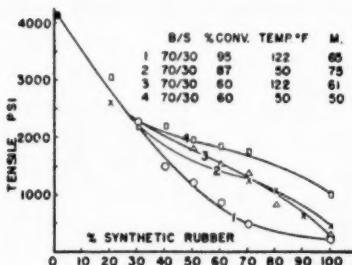


FIG. 1.—Effect of reaction temperature.

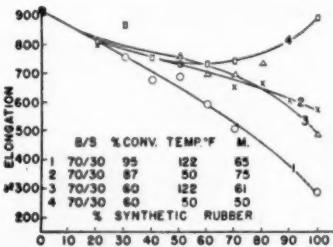


FIG. 2.—Effect of reaction temperature.

between linear and netted species. However, since no simple parameter reflects accurately the gross changes in macrostructure which diene polymers are capable of undergoing, they have been compelled to describe such changes in terms of Mooney viscosity, and are reporting benzene solubility and swell volume of the gel (Table I) for what added information they give.

Effect of polymerization temperature.—Only the polymerization temperature ranges used in current commercial production, 41° to 50° F and 115° to 140° F, have been studied in the present investigation. The tensile strength and elongation results are summarized in Figures 1 to 4. Figures 1 and 2 depict the effect on the properties when medium or high Mooney 70-30 butadiene-styrene polymers prepared at the two temperatures and two conversion ranges, 60 per cent and 85 per cent, are blended with natural rubber. In these, the

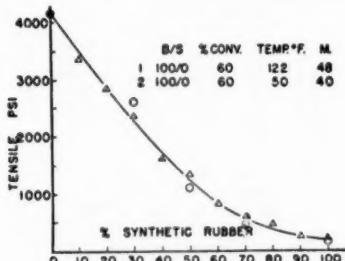


FIG. 3.—Effect of reaction temperature.

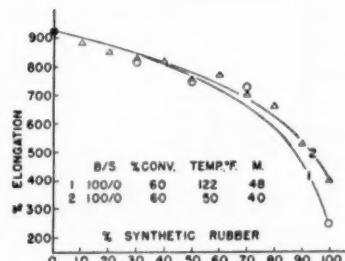


FIG. 4.—Effect of reaction temperature.

incorporation of up to about 30 per cent of all of the synthetics decreased the tensile strengths about equally, the differences between the various rubbers becoming pronounced only at the higher synthetic contents. The superiority of the 70-30 butadiene-styrene cold-rubber latexes in both tensile strength and elongation is evident. Actually, the superiority of the cold rubber polymers in

blends is greater for technological purposes than would be deduced from the graphs, because of their higher wet gel strength. The differences would be rendered somewhat more striking if comparisons were made on some basis representing the total amount of energy to break the sample, which is roughly approximated by the product of tensile and elongation (tensile product). Tensile product is not too widely accepted by the rubber technologist as a measure of stress-strain characteristics and, accordingly, these results have not been depicted graphically.

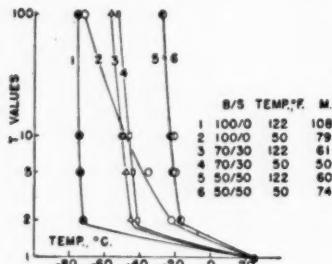


FIG. 5.—Effect of reaction temperature.
60% conversion.

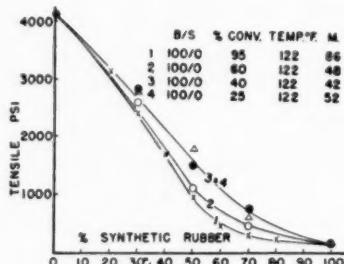


FIG. 6.—Effect of conversion.

Figures 3 and 4 show similar data obtained on the hot and cold medium Mooney 60 per cent conversion polybutadienes. In this case, lowering of the polymerization temperature did not have much effect, and the properties were at a generally lower level than for the styrene-containing polymers.

The solubility and swell volume properties of the butadiene-styrene cold rubber latexes differed substantially from their hot rubber counterparts (see Table I).

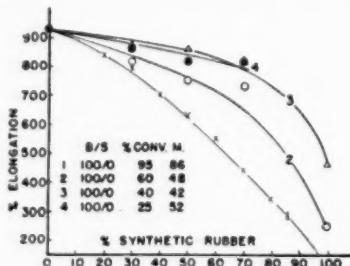


FIG. 7.—Effect of conversion.

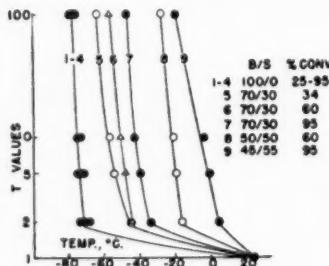


FIG. 8.—Effect of conversion. 122° F.

The effect of polymerization temperature on the low-temperature stiffening properties of polymers of several styrene contents, evaluated in 100 per cent synthetic compositions, is seen in Figure 5. Except for the cold rubber polybutadiene, no significant effects of reaction temperature can be discerned. The apparently anomalous behavior of the cold polybutadiene (curve 2) has been observed in various stocks by many observers, and is attributable to the readiness with which the polymer crystallizes at low temperatures.

Effect of conversion.—The medium-conversion polymers exhibited higher tensile strength than the high-conversion polymers, as shown in Figures 1 and 6. This trend became more pronounced with the 70-30 butadiene-styrene polymers than with the polybutadiene rubbers.

The medium- and low-conversion polymers exhibited higher ultimate elongations than the high-conversion polymers (Figures 2 and 7).

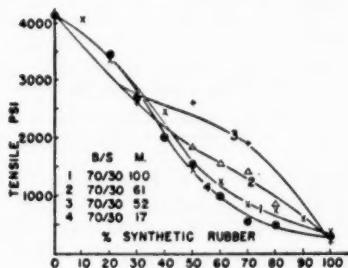


FIG. 9.—Effect of Mooney viscosity.
60% conversion, 122° F.

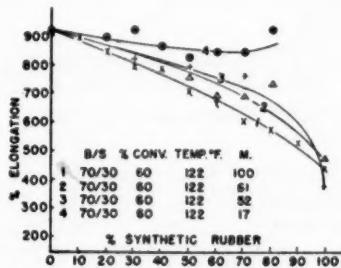


FIG. 10.—Effect of Mooney viscosity.

The degree of conversion had no effect on the low-temperature properties of polybutadiene. The behavior in low-temperature stiffening of the copolymers at varying conversions was accounted for by the variations in their combined styrene content (Table I and Figure 8).

Effect of Mooney viscosity.—With blends of natural-rubber latex and hot synthetic-rubber latex, the tensile strength was optimum for the polymers of medium Mooney viscosity, as shown in Figures 9 and 11. The ultimate elongation increased with decrease in Mooney viscosity with 70-30 butadiene-styrene polymers (Figure 10), whereas the reverse was true with 80-20 butadiene-styrene polymers up to, but not including, the 100 per cent synthetic polymers

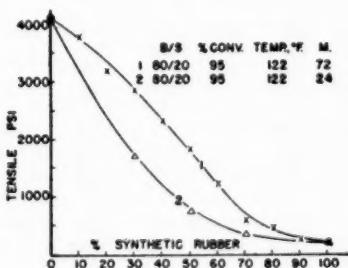


FIG. 11.—Effect of Mooney viscosity.

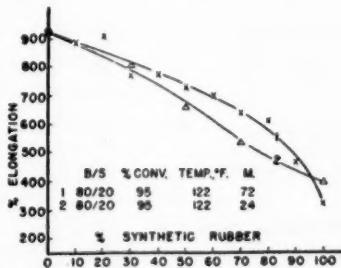


FIG. 12.—Effect of Mooney viscosity.

(Figure 12). The apparent anomaly obtained with the 80-20 polymers, which is contrary to general experience in this laboratory, may be due in part to the fact that they were made under quite different polymerization conditions; the low Mooney sample (Type VII, see Table I) had an unusually tight and high concentration of gel for so low a Mooney plasticity.

Effect of monomer ratio.—When the butadiene-styrene ratio of the synthetic

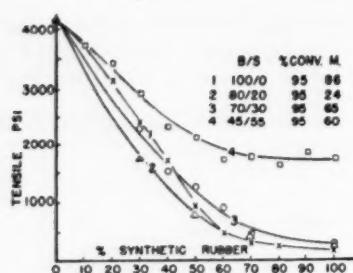


FIG. 13.—Monomer ratio varied. 122° F.

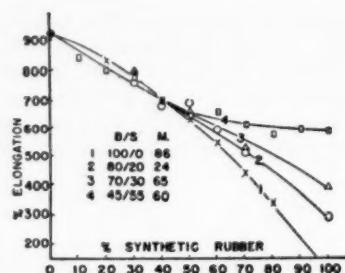


FIG. 14.—Monomer ratio varied. 95% conversion, 122° F.

polymers (122° F polymerization temperature and 95 per cent conversion) was varied from 100-0 to 70-30, the tensile strength of natural-rubber blends was approximately the same for each polymer. The 45-55 butadiene-styrene polymer, however, possessed much higher tensile strength, especially, as is shown in Figure 13, at the higher synthetic levels.

TABLE V
EVAPORATED SHEETS COMPARED WITH MILLED SHEETS

Synthetic rubber	Evaporated sheets				Milled sheets			
	Natural rubber (%)	Synthetic rubber (%)	Ultimate elongation (%)	Tensile strength (lb./sq. in.)		Ultimate elongation (%)	Tensile strength (lb./sq. in.)	
				At break	At 600%		At break	At 600%
100	0	920	4150	600	710	3450	1700	
Polybutadiene	70	30	790	2425	600	630	2250	1850
95% Conversion	50	50	710	1250	550	570	1300	
Hot, MS = 109	30	70	520	300		450	800	
	0	100	150	150		200	450	
Polybutadiene	70	30	860	2800	525	600	2200	2200
60% Conversion	50	50	800	1560	450	520	1550	
Hot, MS = 108	30	70	690	550	350	390	850	
	0	100	250	180		220	500	
Polybutadiene	70	30	830	2350	450	650	2400	1650
60% Conversion	50	50	760	1325	280	640	1750	1300
Cold, MS = 40	30	70	700	565	300	500	700	
	0	100	400	175		300	300	
70-30 Butadiene-styrene	70	30	760	2275	790	650	2650	2000
95% Conversion	50	50	690	1225	650	570	1600	
Hot	30	70	510	450		470	700	
Type V, MS = 65	0	100	290	250		230	280	
70-30 Butadiene-styrene	70	30	810	2300	500	690	3000	1675
60% Conversion	50	50	750	1450	500	600	2200	2200
Hot, MS = 75	30	70	770	625	425	520	1275	
	0	100	470	250		400	750	
70-30 Butadiene-styrene	70	30	870	2200	390	730	2650	750
60% Conversion	50	50	735	1975	600	650	2075	1500
Cold	30	70	745	1775	500	650	1700	1400
X-547, MS = 50	0	100	900	1050	200	420	275	

The ultimate elongation of blends of 50 per cent or more synthetic content increased with increasing styrene content (Figure 14).

It is apparent that the tensile products of these polymers are more nearly an indication of their real value than either tensile strength or elongation considered separately.

The low-temperature stiffening behavior of the 100 per cent synthetic stocks followed the expected trend of increasing in stiffness with increasing styrene content (Figures 5 and 8).

Comparison of evaporated sheets with milled sheets.—A few of the latexes used in this study were examined in a typical gum formula over a range of natural-synthetic ratios. The stress-strain properties were in good agreement at medium and high natural-rubber contents, but at the low natural-rubber contents the tensile strengths of the milled sheets were often higher. The elongation of the evaporated and milled sheets was approximately the same. One exception to this was X-547, which, except at high natural-rubber contents, gave higher tensile strengths and elongations in evaporated sheets than in milled sheets (Table V).

Commercial low temperature latexes.—Figures 15 and 16 depict stress-strain properties of several 50° F latexes which have been produced commercially or have been made available as samples to the trade.

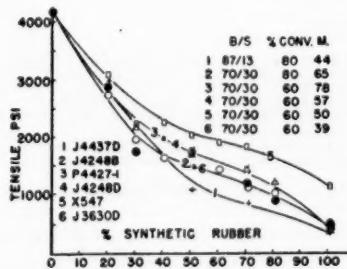


Fig. 15.—Commercial and pilot plant latexes. 50° F.

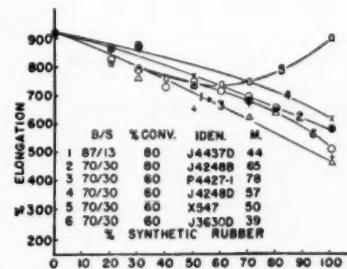


Fig. 16.—Commercial and pilot plant latexes. 50° F.

The values for tensile strength of several of the 70-30 butadiene-styrene polymers were widely divergent, even though the latexes had been made under conditions intended to give equivalent properties (Figure 15).

The ultimate elongations of all the cold rubbers were markedly higher than for their hot rubber counterparts (Figures 2, 4, 10, and 14).

The tensile products of the cold commercial latexes were sufficiently high to make them extremely interesting for industrial utilization.

CONCLUSIONS

When tested in a single standardized procedure for cast latex films, the type of synthetic-rubber latex employed in latex blends containing 70 per cent or more natural-rubber latex had little effect on the stress-strain properties of the mixture.

Cold-rubber latexes imparted higher stress-strain values to blends with natural rubber than did the corresponding hot-rubber latexes. The improvement was particularly noted on comparison of tensile product values.

Low-conversion synthetic polymers produced higher stress-strain properties than high-conversion polymers in blends with natural rubber, even though their tensile strengths in 100 per cent synthetic stocks were approximately equal.

Optimum physical properties were obtained by use of blends with synthetic polymers of medium Mooney viscosity. It is believed that the appearance of an optimum Mooney viscosity is tied in with the necessity of having quite high molecular weight on the one hand, and, on the other, the ability of the particles to knit well, the latter in turn requiring a comparative freedom from tight gel.

Tensile product values increased with increasing styrene content in the synthetic polymer, but, correspondingly, the low-temperature stiffening increased.

The physical properties of a natural rubber stock are far superior to those of any of the synthetic-rubber latexes tested to date. Cold-rubber latexes now in production are an improvement over high-temperature latexes, for example, in wet gel strength but do not approach natural rubber latex in stress-strain properties.

ACKNOWLEDGMENT

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MECHANISM OF THE GELLING OF HEVEA LATEX BY ZINC COMPOUNDS *

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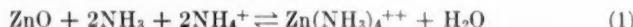
INTRODUCTION

It was observed several years ago by van Gils¹ that fresh latex could be coagulated by addition of small amounts of a soap such as ammonium oleate. The coagulation was attributed to interaction between the soap and free magnesium ions present in the latex. Van Gils has further suggested that the spontaneous coagulation of latex can be explained by the formation of higher fat acids through natural saponification of their compounds. The fat acids are considered to react (at the surface of the rubber particles) with the free magnesium ions, forming a water-insoluble metal soap which causes coagulation of the latex. It will be shown in the present work that a very similar type of interaction can account for the gelation of ammoniated latex by zinc compounds. If the magnesium ions in fresh latex are precipitated as magnesium ammonium phosphate, which occurs when the latex is preserved with ammonia, provided that the phosphate content of the latex is sufficient, the addition of small amounts of soap does not cause coagulation².

Since ammoniated latex has a pH between 10 and 11, a slow but continuous hydrolysis of the proteins, phospholipids, and esters occurs on storage. This results in a large increase in the content of both water-soluble acids and fat acids, with corresponding changes in the stability of the latex³.

The stability of latex towards zinc oxide is markedly affected by the concentration of acids in the latex. This is due primarily to the fact that the solubility of zinc oxide in pure ammonia solutions is very small but increases rapidly as the concentration of ammonium salts in the solutions increases⁴. Thus, in an old latex with a normal ammonia concentration and a high content of water-soluble acids, zinc oxide dissolves readily and causes a corresponding reduction in the stability of the latex, especially on heating. If the concentration of water-soluble acids is naturally low, the solubility of zinc oxide in the latex can be enhanced by degrading the proteins to water-soluble acids by means of trypsin⁵.

The dissolution of zinc oxide in solutions of ammonia containing ammonium salts can be expressed formally by the equation:



Actually, the zinc oxide will first yield zinc ions, which then combine with the ammonia, forming a zinc-ammonia complex. The addition of ammonium salts will lower the hydroxyl ion concentration without lowering the ammonia concentration.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 28, No. 3, pages 144-155, June 1952.

At one time it was suggested by van Nederveen and Houwink⁶ that the gelation of latex by zinc oxide at elevated temperatures was due to the coagulating action of the above bivalent complex. If this explanation were true, one would expect rapid coagulation at room temperature, such as occurs on addition of magnesium, barium, calcium, and similar ions. It is typical of the Kaysam reaction, however, that gelation occurs rapidly only at elevated temperatures. It is important to note that the presence of the bivalent zinc complex ion as such in latex is insufficient to cause rapid gelation.

In the present work, a study has been made of many variables which influence the gelation of latex by zinc compounds, and a new mechanism for the interaction is suggested.

EXPERIMENTAL

The stability of latexes containing different coagulants was observed by measuring the time required for the latex to gel under standard conditions. The latex was contained in aluminum tubing of uniform wall thickness, closed at the bottom end with a cork and immersed in a thermostat. To ensure temperature equilibrium, the latex was stirred mechanically with an aluminum rod, at the end of which was attached two small strips of aluminum in the form of a cross. The stirrer was moved slowly in an up-and-down direction at controlled speed. A support for the aluminum tubes was constructed so that six tubes could be operated simultaneously in the thermostat. The gelation point was easily observed by the setting of the gel around the mixing rod, which resulted in the lifting up of the whole tube out of the thermostat. The gelation process was characterized by the time required for gelation to occur at a constant temperature. The above method differs from that used by Lepetit⁵ and Campbell⁷ in that tubes of aluminum were used instead of glass, which is a poor conductor of heat. Furthermore, the use of ordinary glass test-tubes has the drawback that the thickness of the tubes is seldom constant, and this affects the gelation time. The method described here enables very reproducible gelation times to be obtained.

The zinc or other metal was introduced into the latex, not as solid zinc oxide, but in the form of a solution in aqueous ammonia containing ammonium salts. The use of such preformed complex salts has the advantage that the concentration of dissolved zinc can be accurately controlled. The composition of the complex salt solution is characterized in the present work by the mole ratio of metal oxide, ammonium salts, and ammonia used for preparing the solution. The pH of this solution may vary between 9 and approximately 11.5, depending on the ratio of the ammonium ion concentration to free ammonia.

Complexes can be prepared with a variety of ammonium salts derived from hydrochloric acid, nitric acid, formic acid, acetic acid, lauric acid, oleic acid, glutamic acid, the pseudo-acid nitroethane, etc.

RESULTS

SOLUBILITY OF ZINC OXIDE IN THE SYSTEM $H_2O/NH_3/NH_4Cl$

The experimental conditions chosen were similar to those existing in the water phase of latex, but without amino acids and proteins present.

Ten millimoles (0.814 gram) of zinc oxide was added to 72 cc. of water containing altogether 0.087 gram-atoms of nitrogen, as ammonia and ammonium chloride, with varying ratios of these substances.

By comparison, the aqueous phase of 60 per cent ammoniated latex con-

TABLE I

SOLUBILITY OF ZINC OXIDE IN THE SYSTEM CONSISTING OF WATER, NH_4Cl AND NH_3 AT ROOM TEMPERATURE

ZnO millimoles	NH_4Cl	NH_3	pH	Solid phase remaining
10	20	67	10.8	++++
10	24	63	10.6	++
10	28	59	10.4	+
10	32	55	10.2	+
10	36	51	10.1	-

tains about 67 millimoles of ammonia in 67 cc. of water, and 100 grams of latex rubber require about 0.8 gram of zinc oxide for quick gelation at elevated temperatures. The solubility data for zinc oxide are set out in Table I.

From this experiment we see that, at a pH of about 10.4, the zinc oxide dissolves quickly at room temperature under the conditions adopted.

The purpose of the addition of ammonium salt to latex containing zinc oxide is to decrease the pH to the region where rapid dissolution is possible, without lowering too much the ammonia concentration.

ACTIVITY OF THE ZINC IONS FORMED FROM THE ZINC-AMMONIA COMPLEX AT
ELEVATED TEMPERATURES

A few preliminary experiments were made to estimate the activity of the zinc ions released by the complex salt at higher temperature. An electric cell was made up, consisting of the following parts:

-Zn	Zn^{++}	K Cl 1 M agar	K Cl 1 M	Hg_2Cl_2 Hg	Hg+
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The potential of this cell was measured by compensating with a potentiometer, at temperatures in the range of 20-80° C, and using (1) solutions of zinc sulfate of known molarity, and (2) solutions of a zinc-ammonia complex prepared by diluting a 1 molar solution of zinc oxide in 6 N ammonium nitrate and 2 N ammonia (1:6:2).

Comparison of the data obtained showed that, at 80° C, the activity of the zinc ions released from the complex was about 10^3 to 10^4 times the activity at room temperature, though still small by comparison with the activity in a $10^{-3} M$ zinc sulfate solution at the same temperature.

TABLE 2
GELATION TIMES OF LATEX TREATED WITH TWO TYPES
OF SOAP IN TWO CONCENTRATIONS

Latex	%	Gelation time in minutes	
		After first creaming	After second creaming
Control		3	3
Igepon-T	0.1	6	30
Igepon-T	0.5	>30	>180
Nekal-BX	0.1	3	1.5
Nekal-BX	0.5	2-3	immediately at room temperature

TABLE 3
GELATION TIMES OF IGEPON-T LATEX TREATED WITH AMMONIUM OLEATE

Latex	Gelation time in minutes	
	Before treatment with NH ₄ -oleate	After treatment with NH ₄ -oleate
Igepon T	0.1%	30
Igepon T	0.5%	>180

EFFECT OF TYPE AND CONCENTRATION OF SOAP ON THE GELLING OF LATEX
BY ZINC COMPOUNDS

The natural soaps of latex were displaced by Igepon-T (sodium salt of 2-(*N*-oleyl-*N*-methylamino) ethylsulfonic acid) and, in another sample, by Nekal-BX (isobutylnaphthalene sodium sulfonate). Igepon-T does not form an insoluble zinc soap, whereas Nekal-BX does. Adsorption displacement was carried out in latex diluted to a rubber concentration of 10 per cent, while the soaps were used in 0.1 and 0.5 per cent concentration. The ammonia content was held at about 1*N*; the time of contact was about 20 hours. After creaming with konnyaku flour (0.2 per cent on the aqueous phase), part of the resulting cream was again diluted to a dry rubber content of 10 per cent with the soap solutions under the conditions already mentioned. Adsorption displacement

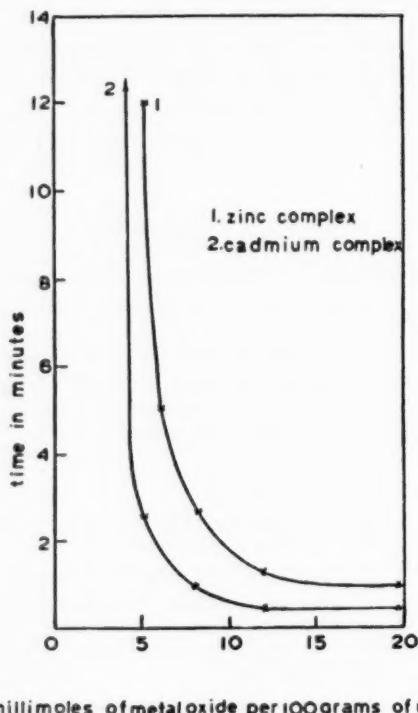


Fig. 1.—Gelation of latex with ammonia complexes of zinc and cadmium.

was again allowed to proceed for about 20 hours, after which the mixture was creamed. The gelation experiments were carried out with 3 per cent zinc oxide on the weight of rubber and with 20 millimoles of ammonium chloride added to 200 grams of cream, the TS of the cream being 50 per cent and the gelation temperature 70° C. The results are given in Table 2.

These results show that as the natural soaps are displaced from the surface of the rubber particles by Igepon-T, the gelation becomes progressively slower. Nekal, however, which reacts with zinc ions yielding an insoluble soap, produces an accelerated gelation. The latex which had been treated with Igepon-T was then subjected to treatment with ammonium oleate in a concentration of 0.5 per cent (once only). The gelling time of the resulting cream was deter-

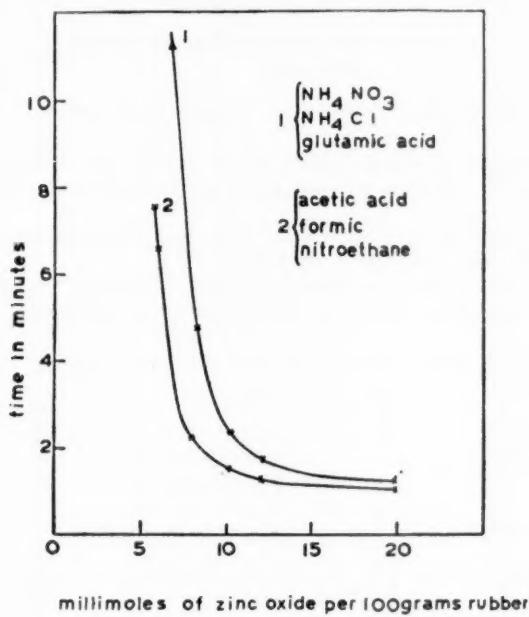


FIG. 2.—Gelation of latex with various zinc complexes.

mined using the methods and conditions already mentioned. Table 3 gives the results obtained.

From this table it can be seen that by displacing the nonreactive Igepon-T by ammonium oleate, the rapid gelling properties of the latex are restored.

From these experiments it is concluded that the nature as well as the amount of soap adsorbed on the rubber particles controls the gelation with zinc oxide.

COMPARISON OF GELATION OF LATEX WITH AMMONIA COMPLEXES OF ZINC AND CADMIUM

It appeared interesting to investigate whether other metal-ammonia complexes would show the property of gelling latex at higher temperatures. The

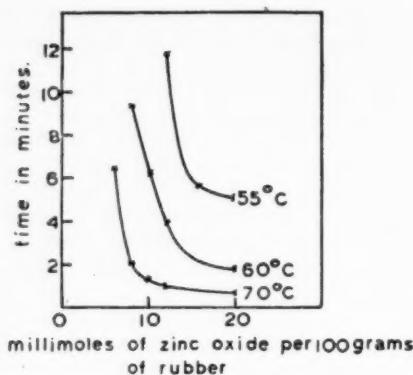


FIG. 3.—Effect of temperature on the gelation with zinc complex.

ammonia complexes of nickel, copper, silver, cobalt, and cadmium were examined. Only the cadmium complex acted in a manner similar to that of the zinc complex.

One-molar solution were prepared of zinc and cadmium containing ammonium chloride and ammonia in the ratios: 1:2:6.

To 60 per cent centrifuged latex increasing amounts of the metals were added as complex salts. Constant volume was not maintained. The gelling

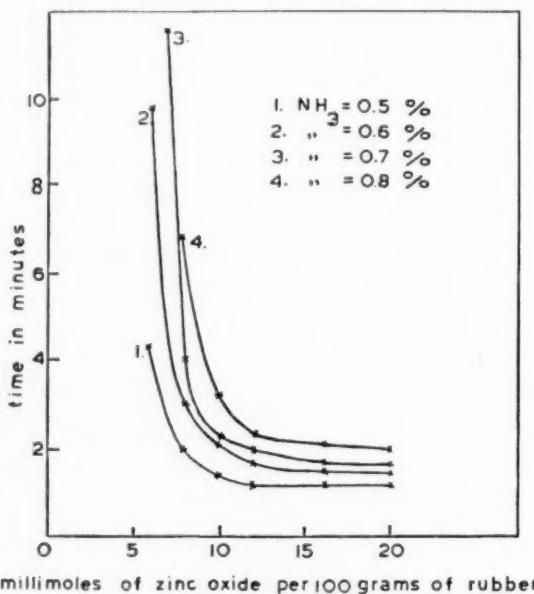


FIG. 4.—Effect of the ammonia content on the gelation with zinc complex.

time, determined at a temperature of 70° C , is shown as a function of the metal concentration in Figure 1.

It can be seen that cadmium causes faster gelling than zinc. However, the most important conclusion is that gelling is not confined to zinc complexes only.

EFFECT OF ANION

Comparative gelation experiments were carried out with complexes prepared by dissolving zinc oxide in ammonia containing the ammonium salts of (1) nitric acid, hydrochloric and glutamic acids, and (2) acetic acid, formic

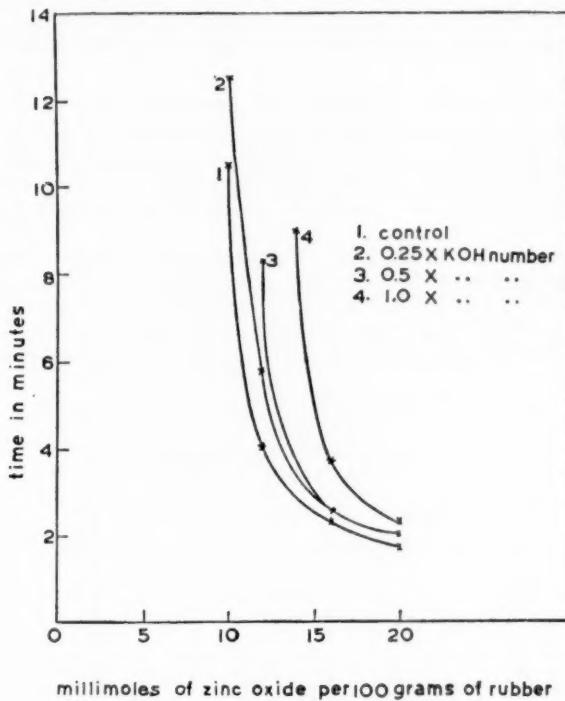


FIG. 5.—Effect of hydroxyl ions on the gelation with zinc complex.

acid and the pseudo-acid nitroethane. The zinc oxide concentration in the complex salt solution was 0.5 molar; the ratio of zinc oxide, ammonium salts, and ammonia was 1:2:6. The gelation temperature was 70° C . The results obtained can be grouped around two curves 1 and 2. More rapid gelation is exhibited by the acids mentioned under group (2) (Figure 2).

EFFECT OF TEMPERATURE

The effect of temperature is illustrated by the following example carried out with a preformed zinc-ammonia complex containing 0.5 molar zinc oxide (1:2:6), with formate as anion. The gelation curve was determined at 50° ,

55°, 60° and 70° C. At 50° C gelation is very slow, even with as much as 0.020 gram-atom of zinc. With increase in temperature, the time of gelation decreases, as shown in Figure 3.

EFFECT OF AMMONIA CONCENTRATION

In order to ascertain the effect of the ammonia content of the 60 per cent centrifuged latex on the gelling behavior, samples of latex were prepared with ammonia concentrations varying from 0.5 to 0.8 per cent on the latex. The dry rubber content was kept constant. As gelling agent a zinc-ammonia complex 2 molar with respect to zinc oxide (1:2:6) was used in increasing amounts. The gelling temperature was 70° C. The results are plotted in graph 4 against time of gelling. It can be seen that an increase in ammonia content retards the gelling.

EFFECT OF HYDROXYL AND PHOSPHATE IONS

Potassium hydroxide was added to samples of latex in an amount equal to its KOH-number (0.73) and also in one-half and one-quarter of this amount. Gelation was brought about as in the preceding paragraph. The gelling curves plotted in Figure 5 show that gelation is retarded by the presence of hydroxyl ions.

In order to determine the effect of phosphate ions, three mixtures were made up consisting of 167 cc. of 60 per cent latex, to which were added, respectively, 5 cc. of water, 5 cc. of a 3 per cent solution of secondary sodium phosphate, and 5 cc. of a 6 per cent solution of this phosphate. To these mixtures increasing proportions of a 2M zinc-ammonium complex (1:2:6)

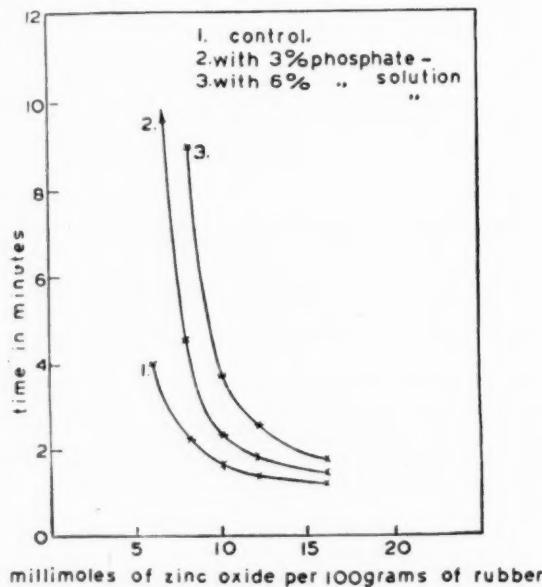


FIG. 6.—Effect of phosphate on the gelation with zinc complex.

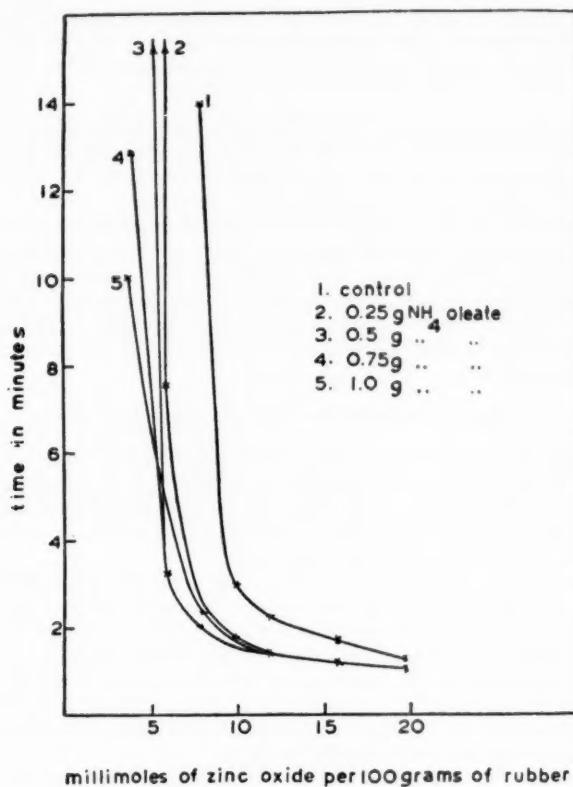


FIG. 7.—Effect of ammonium oleate on the gelation with zinc complex.

were added, and the gelling times determined at 70° C. The gelling curves, plotted in Figure 6, showing that an increase in phosphate content retards gelling.

EFFECT OF THE ADDITION OF AMMONIUM OLEATE

Samples of latex containing increasing amounts of ammonium oleate were examined at 70° C, using a molar solution of zinc-ammonium complex (1:2:5) as gelling agent. Figure 7 illustrates the accelerated gelling caused by the added soap.

DISCUSSION

It was pointed out in the introduction that the complex cation $ZN(NH_3)_4^{++}$, which is formed by the addition of zinc oxide and ammonium salts to ammoniated latex, does not cause rapid gelation of the latex at room temperature. The compounds formed by the above cation with higher fat acids are particularly interesting, since they are very soluble at room temperature but (as we have recently observed) are reversibly decomposed on heating, giving simple zinc soaps which are insoluble. On cooling the system, the zinc soaps are

taken into solution again as soluble zinc-ammonium soaps. Expressed in terms of the cations involved, the reaction is:



On heating, the equilibrium shifts to the right, thereby increasing the zinc ion concentration. Measurements of the activity of the simple zinc ions in a solution of zinc-ammonium nitrate at temperatures between 20° and 80° C reported in this paper confirm the above equilibrium shift.

An explanation of the gelation of latex by zinc compounds can now be suggested. On heating a latex mixture containing a zinc-ammonia compound, free zinc ions are released which react chemically with the higher fat acids adsorbed on the rubber particles, forming an insoluble zinc soap. The formation of a firm gel could be accounted for if the bivalent zinc ions linked up adjacent rubber particles by combining with one fatty acid molecule from each of two adjacent particles, *i.e.*:



This suggested mechanism is in good agreement with the results obtained for latexes containing an adsorbed film of Igepon-T, which does not form an insoluble zinc salt; gelation of the latex is then greatly retarded, as shown in Table 2. The original fast gelling properties of the latex can be restored by substituting ammonium oleate for Igepon-T.

The increase of gelling time caused by the presence of hydroxyl or phosphate ions can be attributed to their interaction with some of the zinc ions, yielding insoluble zinc hydroxide or phosphate, which is then no longer available for reaction with fat acids adsorbed on the rubber particles.

The concentration of the ammonia is very important, since this influences the position of the equilibrium between the zinc-ammonia complex and the zinc ions (Equation 2). A high ammonia concentration retards gelation, as the zinc ions are forced back into the complex.

The presence of ammonium salts containing different anions (nitrate, acetate, etc.) affect the time of gelation to different extents (Figure 2). Further work is required to explain adequately the influence of the different anions. It is our intention to continue investigations along the lines described in the present paper with a view, if possible, to establishing new methods for the evaluation of latexes differing in chemical stability and in the degree to which decomposition of no-rubber components has taken place.

SUMMARY

Zinc oxide is known to be soluble to a certain extent in ammoniated Hevea latex. The solubility may be enhanced by several means, such as the addition of ammonium salts, and is due to the formation of zinc-ammonia complexes. The complexes themselves have no coagulating power. When heated, however, zinc ions are produced by dissociation of the complexes, and these ions react chemically with the adsorbed soap on the rubber globules, forming an insoluble zinc soap which links up all the rubber globules into a gel.

Evidence in favor of the proposed mechanism was obtained by displacing the adsorbed natural higher fat acids of the rubber particles by a soap which does not form an insoluble zinc soap, such as Igepon-T. A latex treated in this manner does not gel when heated with zinc oxide and ammonium chloride at

70° C. By displacing the Igepon-T with ammonium oleate, the original rapid gelation is restored.

Depending on the concentration of zinc ions available at room temperature and the amount and types of higher fat acids on the latex particles, thickening or even gelling may occur at room temperature.

The above interpretation of the reaction mechanism may lead to new methods for the evaluation of latex.

ACKNOWLEDGMENT

This work forms part of the program of fundamental research on latex problems undertaken by the Rubber-Stichting of Delft, Holland, under the management of H. C. J. de Decker. Our thanks are due to (Miss) N. G. W. J. van Rij for assistance in the experimental work.

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WATER VAPOR PERMEABILITY AND SORPTION OF HEVEA LATEX FILMS *

WILLIAM W. BOWLER

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It has been recognized for many years that Hevea latex films prepared from vulcanized latex must differ greatly in structure from such films when vulcanized after drying. Of particular industrial importance is the fact that films from vulcanized latex (prevulcanized films) are very weak before complete drying, yet, when dry, their tensile strength compares favorably with that of films which are vulcanized in the dry state (dry vulcanized films). Hauser¹, using a micromanipulator, discovered that during liquid vulcanization the Hevea latex particle changes from an easily deformable plastic mass to an elastic particle, which, in overvulcanization becomes crumbly. As a result of a later investigation, Hauser, le Beau, and Kao² advanced the theory that prevulcanized films depend for their strength on the formation of sulfur linkages between particles, and that these bonds cannot form until drying has proceeded far enough to diminish Brownian motion and to allow the individual particles to approach each other more closely than is possible in the wet state.

After a thorough study of vulcanized latex, van Dalfsen³ stated that in fresh latex, which has a thick adsorption layer on the rubber particles, the high tensile strength of prevulcanized films is a result of secondary van der Waals forces between the individual particles. These forces are large when the particles approach each other closely in a dried film, but are necessarily much weaker in a wet film when the particles are protected by a swollen adsorption layer. In old or purified latex, with a thinner adsorption layer, sulfur bonds may form from one particle to the next, according to van Dalfsen. In a film vulcanized in the dry state, on the other hand, the tensile strength depends to a great extent on the primary valence forces of sulfur bonds. These sulfur bonds not only cross-link the long, randomly coiled molecules within each particle, but join molecules from different particles as well. More recently, Humphreys and Wake⁴ stated that in prevulcanized films the cohesion between particles can only be due to the van der Waals or secondary valencies.

Since van Dalfsen⁵ found that prevulcanized and dry vulcanized films differ radically in water vapor permeability, an investigation of this phenomenon was undertaken. It was hoped that further permeability studies would yield information, not only on the mechanism of water vapor permeation through latex films, but also on the structure of the various types of films.

The permeation of water vapor through a rubber film can be considered to consist of two processes, the sorption of water vapor at one side of the film, followed by diffusion of water vapor through the film, and evaporation at the other side. In the ideal case, the number of grams of water vapor, Q , passing

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through the area, A , of a film of thickness x in time t is given by the relation:

$$Q = P \cdot \frac{A \cdot t \cdot \Delta p}{x} \quad (1)$$

where Δp is the vapor pressure difference across the film and P is the constant of proportionality called the permeability constant. P has the dimensions $M \cdot L/L^2 \cdot t$ (pressure) and in this study is expressed as grams/cm./second/cm. of mercury. For the sorption of water vapor by rubber, the sorption coefficient, S , can be defined by the expression:

$$C = S \cdot p \quad (2)$$

where C is the concentration of water in grams of water per cc. of rubber, and p is the aqueous vapor pressure in cm. of mercury. The constants, P and S , can be related⁶, in the units mentioned by the expression:

$$P = D \cdot S \quad (3)$$

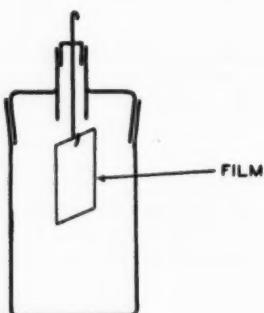
where D is the diffusion constant. However, D can only be calculated from P and S values when the processes represented in Equations 1 and 2 are followed. The permeation and sorption processes were first studied, therefore, to determine how closely these two expressions are followed for latex films.

EXPERIMENTAL

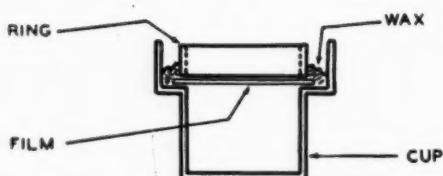
The method used to study the permeability of latex films to water vapor consisted of sealing a film across an aluminum cup containing water or a saturated salt solution, placing the cup in a desiccator containing aluminum oxide as desiccant, and determining the rate at which the cup lost weight when the desiccator was immersed as far as the rim in a constant temperature bath. The aluminum cups (Figure 1) were machined from block aluminum, and were similar to the design suggested in the A.S.T.M. procedure for testing permeability of plastic materials⁷. The circular area through which permeation took place was 7.92 sq. cm. Water or a saturated salt solution provided a known vapor pressure, p_1 , on the lower side of the film, and the desiccant a vapor pressure, p_2 , of zero on the other side. The vapor pressure difference across the film, Δp , was then $\Delta p = p_1 - p_2$. A few experiments were made with the desiccant in the cup and the aqueous solution in the desiccator. Both directions of vapor flow yielded the same rate for a given film in every test. The thickness of the film was measured by means of a dial gage graduated to 0.001 inch. There was no detectable change of thickness during an experiment.

To prepare a cup for a run, water was first placed in it or, if a salt solution was used, the solution was placed in a small glass container in the bottom of the cup. A circular film, cut slightly larger than the 1.25-inch diameter opening, was placed over the mouth, and an aluminum ring, having an inside diameter equal to that of the cup, was placed on the film and centered by means of a template fitting the raised outer rim of the cup. A heated beeswax-resin mixture was poured around the edge of the ring to seal off the edge of the film. The complete assembly, cup, film, and ring, was then placed in the desiccator. A fan was inserted in the top of the desiccator through a mercury seal in order to keep the air in motion and retain a water vapor pressure of effectively zero at the upper surface of the film. Varying the speed of rotation of the fan did not alter the rate of permeation as long as a gentle flow of air over the film was

maintained. Weighings were recorded only after a constant equilibrium rate of vapor flow was established; this usually required about 3 days. Weighings were then made after successive 24-hour periods. On most films five weighings were sufficient to yield a reliable average. All measurements were made at $25.0^\circ \pm 0.3^\circ \text{ C}$, except in the experiments in which the effect of temperature was studied. It is recognized that, with no circulation of air inside the cup, the vapor pressure, p_1 , at the lower surface of the film might be less than that corresponding to the saturated aqueous pressure of the solution in the cup. However, the surface of the liquid was in all cases less than 0.5 cm. from the



SORPTION BOTTLE



PERMEABILITY CUP

FIG. 1.—Permeability cup with ring; sorption bottle.

film, and at the low rates of permeation encountered the error from this source was assumed to be negligible. Increasing the distance from the film to the surface of the solution in the cup to 1.0 cm. did not alter the permeation rate.

Sorption measurements were made by the method of Evans and Critchfield⁸, in which a dry film is suspended by a hook in a bottle (Figure 1) containing water or saturated salt solution supplying an atmosphere of known aqueous vapor pressure. Weighings were made by placing the bottle on a saddle across the pan of an analytical balance and suspending the wire holding the film from the end of the balance beam. When constant weight was attained, the sorption coefficient was calculated from Equation 2.

The films were prepared by pouring the latex, strained through cloth to remove coagulum and air bubbles, directly onto glass plates from a beaker, and allowing the film to dry at room temperature. Ammoniated, once-centrifuged natural latex, approximately 5 months old and of 60 per cent dry rubber content, was used for the casting of most films. Basic compound as follows:

	Parts by weight (dry)
Latex rubber solids	100.0
Sulfur	1.75
Zinc diethyldithiocarbamate (Ethyl Zimate)	0.5
Zinc salt of mercaptobenzothiazole (Zenite)	1.0
Di- β naphthyl- <i>p</i> -phenylenediamine (Agerite white)	0.25
Zinc oxide	3.0
Potassium hydroxide	1.0

Prewulcanization was ordinarily carried out by allowing the compounded latex to stand at room temperature for 3 weeks; the film was vulcanized in the dry state by heating at 100° C for 1 hour.

From ten determinations on films of slightly different thickness cast from one uncompounded latex, using water to supply a Δp value of 2.38 cm. of mercury, the average value of P was 3.19×10^{-10} grams/cm./second/cm. of mercury, and the probable error of a single observation, $\pm 0.675 (\Sigma d^2/n - 1)^{1/2}$, was 0.215×10^{-10} . Consequently it was decided that three determinations on one film would yield results of sufficient accuracy for the present study; all measurements were made in triplicate.

RESULTS

The permeability of latex films was first studied as a function of the several variables in Equation 1. There can be no question of the direct proportionality between Q and t , since assembled cups lost weight at a constant rate after the initial adjustment period. Likewise, when cups of different sizes were used, the permeability constant was found to be independent of the area. Schultz, Miers, Owens, and Maclay⁹ found, in an investigation of thin pectinate films, that P varied with A and attributed this effect to the inability of the desiccant to take up water rapidly enough when A was large. This difficulty was not

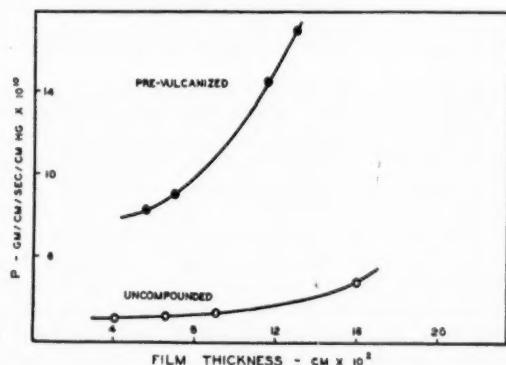


FIG. 2.—Effect of film thickness on permeability constant, P ; $\Delta p = 2.38$ cm. hg.

encountered in the present study because of the relatively low rate of permeation through the much thicker latex films.

The effect of film thickness, x , on the permeability constant, P , is shown in Figure 2 for a prevulcanized film and also for an uncompoounded film. Each point is the average of several determinations. For the uncompoounded film, P varies only slightly with film thickness over a wide range of thicknesses, but P increases greatly with thickness with prevulcanized films. Dry vulcanized films are entirely similar in their behavior here to uncompounded films, but the difference in behavior of the prevulcanized films is an indication that water vapor permeation in these films proceeds by a different mechanism. In all subsequent work, only those films were used whose thicknesses were between 0.04 and 0.06 cm.

The effect of Δp on the permeability constant for a prevulcanized and an uncompounded film is shown in Figure 3. Here again, P is nearly independent of

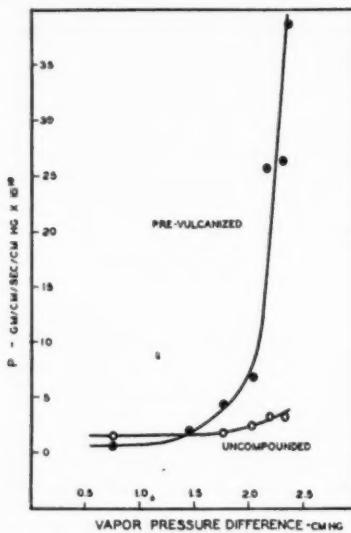


FIG. 3.—Effect of vapor pressure difference on permeability constant, P ; $\Delta p = 2.38$ cm. hg.

Δp for uncompounded films, but for prevulcanized films this is true only at Δp values below 1.5 cm. of mercury. Above this value P increases very rapidly with Δp . In order to work in a region in which the permeabilities of these two types of films are of significant difference, then, it was decided in all subsequent experiments to use a saturated solution of potassium nitrate, giving an aqueous pressure of 2.22 cm. of mercury at 25.0° C. Since this is outside the region in which P is independent of Δp , Equation 1 is not followed for prevulcanized films, and P is not a true proportionality constant. Hence in what follows, the value calculated from Equation 4 as P is designated as P^l to show that it is limited to the above specific conditions. A pressure slightly below that corresponding to saturation was found to increase the reproducibility of the results on a single film, but the Δp value of 2.22 cm. of mercury is within the region where P^l for prevulcanized films is very sensitive to small changes in Δp , and

results on these films consequently varied from film to film. In another experiment with prevulcanized films P varied with the magnitude of p_1 and p_2 as well as with their difference, Δp . A Δp value given by low values of p_1 and p_2 yielded a lower value of P than the identical Δp value given by high values of p_1 and p_2 . The different behavior of prevulcanized and uncompounded films at varying Δp values is additional evidence for the existence of different structures in these two types of films. The most reasonable explanation for this difference in behavior is that diffusion takes place in prevulcanized films through capillary openings, which, if present at all in uncompounded or dry vulcanized films, are much smaller because the relative softness of unvulcanized rubber permits the latex particles to flow together on drying.

No significant effect on permeability could be observed when films were electrodeposited or coagulant-dipped rather than cast, when the latex was diluted before casting, or when the ammonia content of the latex was varied.

The effect of vapor pressure on the sorption of water vapor by uncompounded, dry vulcanized, and prevulcanized films is shown in Figure 4. Since

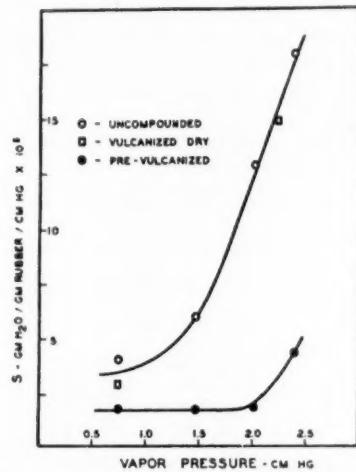


FIG. 4.—Effect of vapor pressure on sorption coefficient, S ; temperature = 25° C.

both uncompounded and dry vulcanized films have larger S values than do prevulcanized films throughout the range studied, the difference must be attributed to a fundamental difference in structure of the prevulcanized films, rather than to the effect of compounding ingredients or to the altered nature of the polymer after vulcanization. The explanation for the lower sorption of prevulcanized films is not known.

As shown in Figure 2, the permeability of prevulcanized films is greater than that for uncompounded films. Yet in the sorption experiments, prevulcanized films were found to sorb considerably less water per gram of rubber. Since the permeation process consists of sorption and diffusion, the actual diffusion rate of water through prevulcanized films must be considerably greater than that for uncompounded films and dry vulcanized films in order to offset the effect of the decreased sorption in prevulcanized films. This is an indication that the

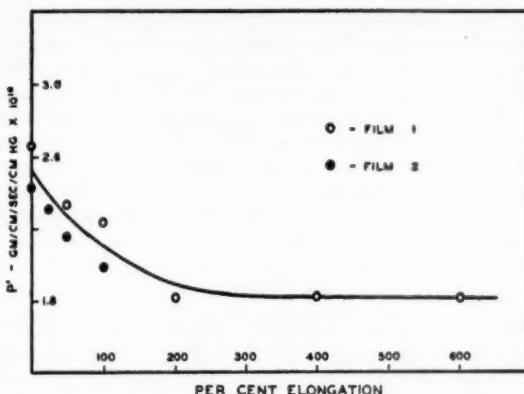
difference in structure between the two types of films is actually very great. Since the permeability of prevulcanized films does not follow Equation 1, and the sorption of water vapor by uncompounded and dry-vulcanized films does not follow Equation 2, it is not possible to calculate a true diffusion constant by means of Equation 3.

The permeability, P^1 , of various films is shown in Table I. An uncompounded film cast from the 5-month old latex had a permeability under the conditions of the test of about 2.6×10^{-10} grams/cm./second/cm. of mercury, whereas this value was decreased about 25% with the 6-year old latex. However, since these were different latexes, the difference cannot be definitely attributed to the age of the latex. Van Dalsen⁵ found that film permeability

TABLE I
EFFECT OF AGE OF LATEX, PRESENCE OF COMPOUNDING INGREDIENTS, AND
FILM TREATMENT ON PERMEABILITY OF LATEX FILMS
(Temperature = 25.0° C; $\Delta p = 2.22$ cm. Hg)

Latex used	Treatment	P^1 (g./cm. sec./cm. Hg $\times 10^1$)
Uncompounded, 5 months old	No cure	2.6
Uncompounded, 2 years old	No cure	2.0
Uncompounded, 6 years old	No cure	1.7
Basic compound	No cure	2.8
Basic compound less S	No cure	2.6
Basic compound less ZnO	Dry cure, 100° C	1.8
Basic compound	Dry cure, 100° C	1.9
Basic compound plus 4.4 parts/100 KCl	Dry cure, 100° C	1.9
Basic compound plus 0.5 part/100 casein	Dry cure, 100° C	1.9
Basic compound plus 1.0 part/100 potassium oleate	Dry cure, 100° C	2.4
Basic compound plus 3.3 parts/100 KOH	Dry cure, 100° C	11
Basic compound	Wet cure, 1 day, 25° C	4.8
Basic compound	Wet cure, 4 days, 25° C	11
Basic compound	Wet cure, 19 days, 25° C	24
Basic compound	Wet cure, 45 days, 25° C	26
Basic compound	Wet cure, 21 days at 25° C (film soaked in water 1 week)	2.5
Basic compound	Wet cure, 2 minutes, 78° C	20

increased with the length of storage of the latex. With the 5-month old latex, compounding and heating, with or without zinc oxide, also reduced the permeability about 25 per cent. Addition of potassium chloride and casein did not alter the permeability of dry cured films; addition of potassium oleate increased P^1 about 25 per cent and addition of potassium hydroxide, about 500 per cent. Curing latex in the wet state at room temperature for this particular compound increased the permeability for about 21 days, after which no significant increase took place. A wet cure at an elevated temperature had a similar effect, although heating for more than 2 minutes at 78° C could not be accomplished without the presence of added stabilizer because of coagulation of the mixture. The permeability of a prevulcanized film was reduced to about one-tenth the original value by soaking in distilled water for 1 week; the per-

FIG. 5.—Effect of stretching on permeability of uncom-pounded films; $\Delta p = 2.22$ cm. Hg.

meability of uncom-pounded and dry vulcanized films was not altered by such soaking. The large increase in permeability of pre-vulcanized films with increasing pre-curing time can be attributed to the gradual stiffening of the rubber particles with vulcanization.

Data illustrating the effect of stretching on the permeability of two uncom-pounded films are plotted in Figure 5. These films were stretched at various

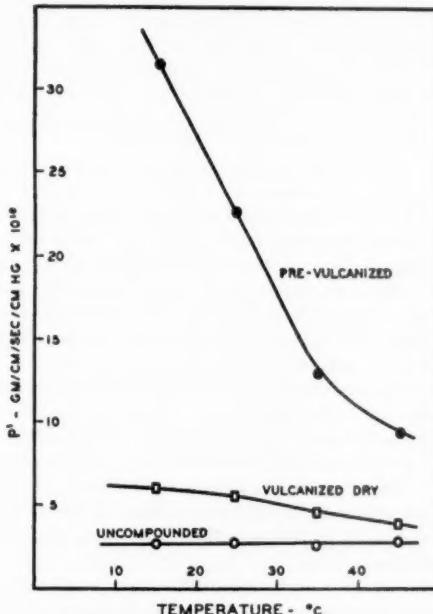


FIG. 6.—Effect of temperature on permeability.

elongations for 1 hour and relaxed for 1 day before the permeability was measured. Under these conditions, crystallization would not be expected to play any important part in the process. The length of time during which the films were stretched was found to have no effect on the subsequent permeability. A film cured after drying suffered no change in permeability after stretching.

In Figure 6 are plotted the measured P^1 values for uncompounded, dry vulcanized, and prevulcanized films at four different temperatures from 15° to 45° C. The difference in the behavior of prevulcanized films is striking and indicates again that prevulcanized films are significantly different in structure from uncompounded and dry vulcanized films.

DISCUSSION

According to Doty, Aiken, and Mark⁶, three types of diffusion through polymer films can be recognized: (1) gaseous diffusion through capillary holes; (2) activated diffusion through the polymer itself; and (3) activated diffusion through capillary holes whose walls are lined with active centers of high adsorption power. It seems reasonable to assume that diffusion takes place in prevulcanized films primarily by this third mechanism, since it is likely that large capillaries, lined with hydrophylllic material, exist in such films as a result of the relative stiffness of the vulcanized rubber particles. This assumption would explain the great increase in the permeability constant with film thickness for prevulcanized films. It is only with pure gaseous diffusion, with no forces of attraction between diffusing molecules and the film, that P would be expected to be independent of film thickness. This assumption would also explain why, for prevulcanized films, P varies with the magnitude of p_1 and p_2 . At low values of p_1 and p_2 the capillaries are lined mainly with hydrophylllic surface material, whereas at high values of p_1 and p_2 with adsorbed water molecules and diffusion could conceivably be much greater through such water-lined capillaries. Likewise the reduction in permeability of prevulcanized films after soaking in water would follow as a result of the washing out of the hydrophylllic material containing the active centers for adsorption.

On the other hand, diffusion in dry vulcanized films probably takes place by an activated diffusion mechanism of a different type, the water molecules moving through temporary "holes" which do not pre-exist, but are the result of thermal movements in the molecules of the materials composing the film. This type of diffusion undoubtedly takes place through both rubber polymer and the adsorbed layer. The lower sorption of water vapor by prevulcanized films may be a result of the continual desorption of water molecules into the large capillary spaces. Such desorption is impossible in uncompounded or dry vulcanized films, which do not have these large capillaries.

In uncompounded films, diffusion probably takes place by essentially the same mechanism as in dry vulcanized films. However, small capillaries, probably destroyed by heating in dry vulcanized films, must exist in uncompounded films, and some diffusion would then occur by the same mechanism as that in prevulcanized films. The decrease in permeability of uncompounded films on stretching would then result from the destruction of these residual capillary spaces, and the permeability of the stretched film tends to fall to the value expected for a dry vulcanized film.

The effect of temperature on permeability can be attributed, at least in part, to a difference in the energy of activation for the two different diffusion processes. This temperature effect may also result from a positive temperature

dependence of desorption of water molecules from active centers into the larger capillaries of prevulcanized films.

The question of whether the strength of prevulcanized films is due to secondary forces between the individual latex particles or to sulfur linkages between the particles is a difficult one. At first glance, one would expect that a prevulcanized film, if secondary forces between the particles are responsible for its strength, would resemble an un compounded film in stress-strain properties. Actually a prevulcanized film is more nearly similar to a dry vulcanized film, in which there is present a three-dimensional network of primary valence bonds. Humphreys and Wake⁴ offer as evidence against the formation of interparticle sulfur bonds the collapse of a prevulcanized film into discrete particles when swollen in benzene. With films which are several months old, however, there is not such a great difference in behavior between those prevulcanized and those dry vulcanized, on swelling in benzene. Both types of films swell, become weaker, and recover a great part of their strength on drying. The prevulcanized film becomes slightly weaker in the swollen state but crumbles on the application of large shearing stresses only to a slightly greater extent, than the dry vulcanized film. When a vulcanized latex dries, sulfur and the other compounding ingredients are deposited at the interfaces between particles. The extent to which sulfur bonds form from one particle to the next would seem to depend on the amount of interfering adsorption material present and on the subsequent treatment of the film. If little or none of such interfering material is present, it seems difficult to suppose that interparticle sulfur bonds would not form on subsequent heating of the film, or even on standing at room temperature for a sufficient length of time. If such sulfur bridges do exist between particles, then the problem of explaining the high tensile strength of prevulcanized films is much less difficult, since both prevulcanized and dry vulcanized latex films then possess an essentially similar primary valence network, despite the presence of larger capillary openings in the γ -vulcanized film. It would not be necessary for bonds to form at every interface between particles for a complete three-dimensional network to exist.

SUMMARY

A considerable structural difference exists between Hevea latex films vulcanized after drying and those vulcanized in the latex state. Since these two types of films differ considerably in water vapor permeability and sorption, a careful study has been made of these phenomena. The weight of water permeating an un compounded film was inversely proportional to the thickness of the film over a wide range of thicknesses, and directly proportional to Δp , the vapor pressure difference across the film, except at very high values of Δp . However, films cast from vulcanized latex were much more permeable to water vapor, sorbed considerably less water, and had a greater negative temperature dependence of permeability than un compounded or dry vulcanized films. These experiments indicate that diffusion takes place in prevulcanized films by an activated diffusion through capillary holes and in dry vulcanized films by an activated diffusion through the polymer itself or the adsorption layer.

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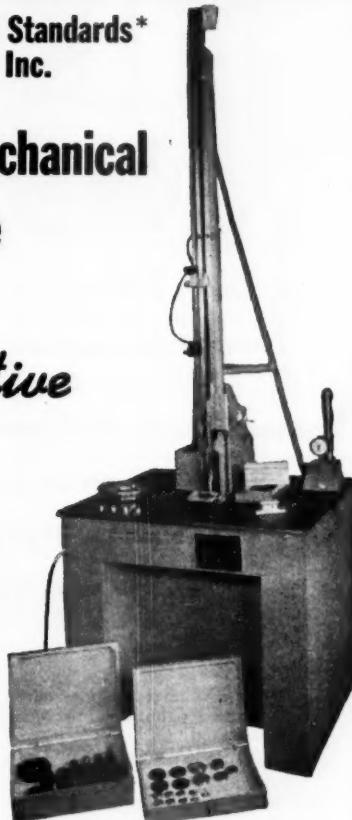
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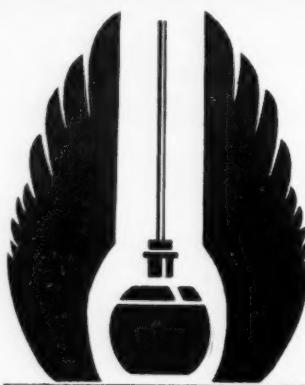


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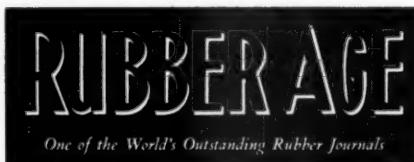
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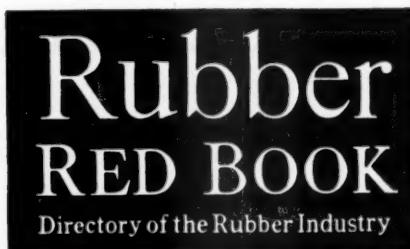


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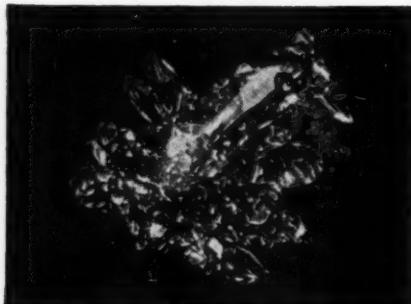
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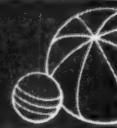
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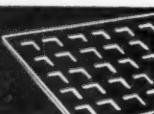
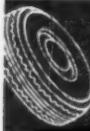


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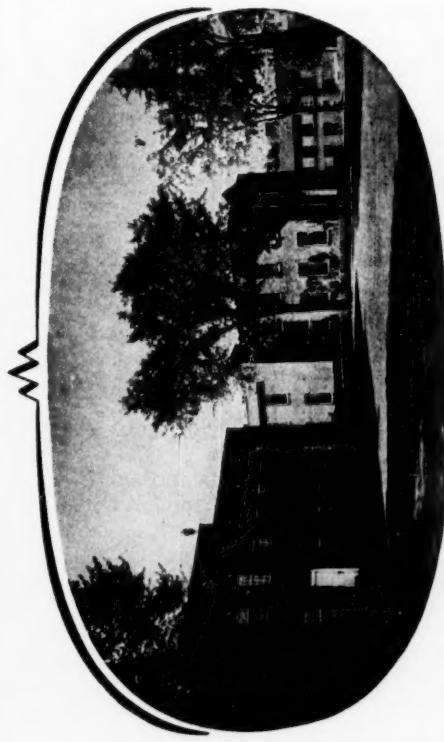
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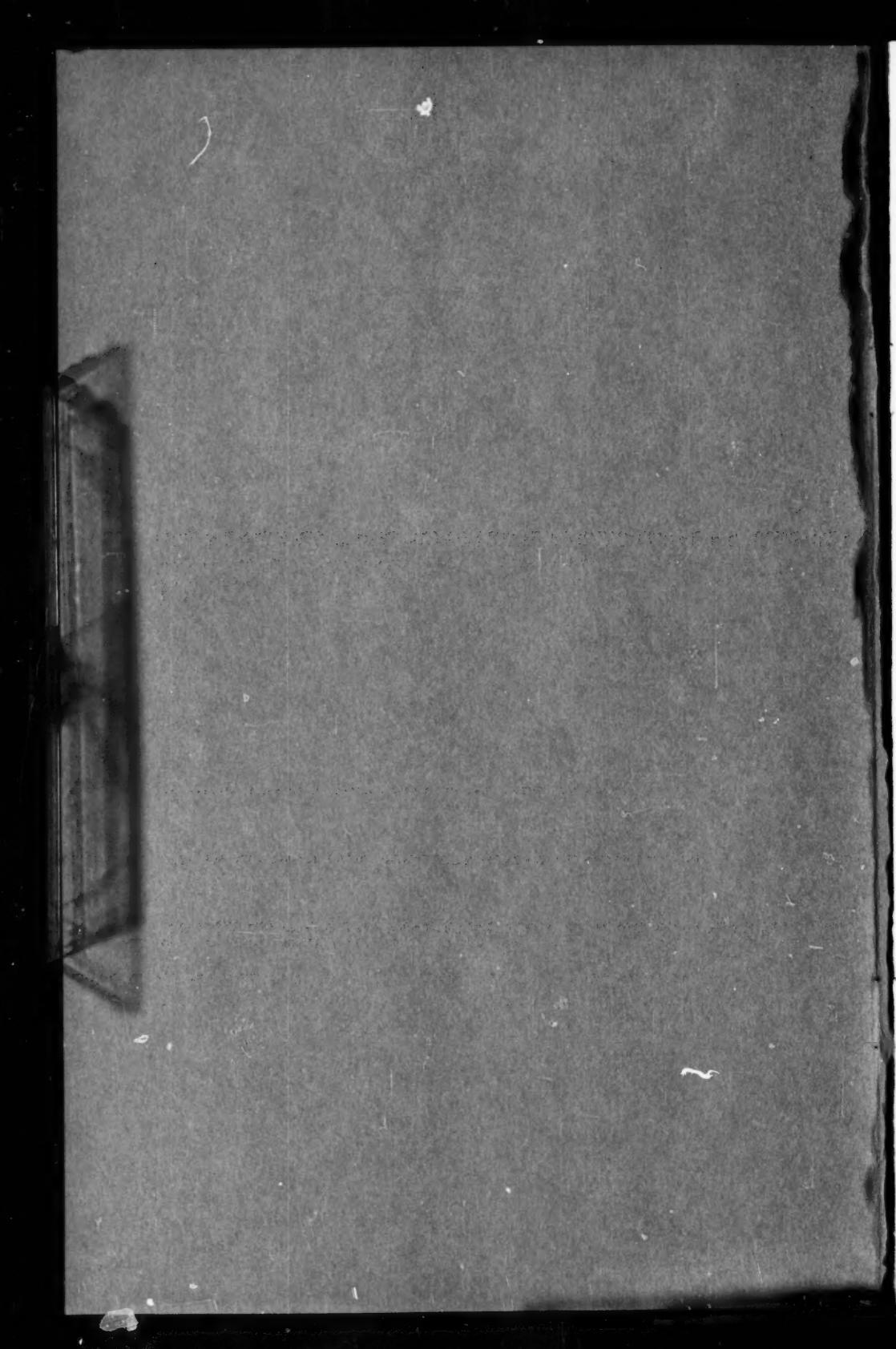
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WURTZ, JACK, 1100 N. Walnut Grove Ave., San Gabriel, Calif. (Arrowhead Rubber Co.)
WYROUGH, GEORGE J., 102 School Lane, Trenton, N. J. (R. E. Carroll, Inc.)

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*YOKOI, KEIRO, 2250 Shinjuku Zushi-machi, Kanagawa Pref., Japan (Yokohama Rubber Co.)
YORAN, CALVIN S., 713 Dodge St., W. Lafayette, Ind. (Brown Rubber Co.)
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*YOUmans, ROBERT A., Shorefront Pk., South Norwalk, Conn. (R. T. Vanderbilt Co.)
YOUNG, DAVID W., 617 Salter Pl., Westfield, N. J.

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YOUNG, J. H., 3902 S. Harmon St., Marion, Ind.
YOUNG, KENNETH C., 35 Drift St., New Brunswick, N. J. (Industrial Tape Corp.)
*YOUNG, RICHARD B., Beacon, Mattapoisett, Mass. (Acushnet Process Co.)
YOUSE, LAWRENCE K., 67 Abbotsford Rd., N. Plainfield, N. J. (Kentile, Inc.)

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*ZIMMERMAN, ELMER W., 6708 - 46th St., Chevy Chase, Md. (Nat'l Bur. of Standards)
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ZMIJEWSKI, WALTER J., 16 Devereux St., Marblehead, Mass. (LePage's, Inc.)
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